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Polyurethane Coatings from Soy-Based Polyols

By

Xiaolan Jin

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read and recommend to the faculty of Gradate Studies and Research for acceptance, a thesis entitled **Polyurethane Coatings from Soy-based Polyols** submitted by Xiaolan Jin in partial fulfillment of the requirements of the degree of **Master of Science in Chemical Engineering.**

Abstract

Polyurethane (PU) is a class of materials that are used in a variety of industrial applications and products in our daily life. The demand for PU has increased considerably over the past couple decades due to the increasing construction activities in the third world countries. In general, polyurethanes are synthesized by reacting polyols with diisocyanates, both of which are petroleum-based raw materials. In recent years, due to various environmental concerns, the use of polyols from renewable agriculture resources, such as soybean oil, for PU synthesis has been growing. This trend is relevant to us since such inexpensive raw materials are abundant in Canada. In this study, several selected soy-based polyols made from soybean oil were used to synthesize PU in order to determine their suitability for being used as coating materials. In particular, soy-based polyols with 2 and 3 hydroxyl groups per molecule were reacted with two commonly used polyisocyanates (aliphatic and aromatic) at a curing temperature of 60 ^{o}C. The performance of the resultant coatings was judged based upon their adhesion strength to stainless steel, abrasion resistance and water resistance. The results were compared with the coatings made by synthetic polyester-based polyols with similar hydroxyl numbers. The glass transition temperatures and Fourier transform infrared spectra of selected samples were also obtained. It was found that the soy-based polyols used are suitable for coating applications. Effects of the molar ratio of polyisocyanate to polyol on the coating performance were also investigated. It was found that as the molar ratio increased, in many cases, the abrasion resistance and water resistance of the resultant coating increased.

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Symbols

ASTM	American Standard Testing Method
DABCO	Diazabicyclo octane
DBTDL	Dibutyltin dilaurate
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetty
E.W.	Equivalent weight
f	Number of functionality
FTIR	Fourier Transform Infrared
HDI	1,6-hexamethylene diisocyanate
$H_{12}MDI$	4, 4'-dicyclohexyl methane diisocyanate
M_c	Molecule weight between crosslinking points
MDI	4, 4'-diphenyl methane diisocyanate
NCO	Isocyanate group
OH	Hydroxyl group
PBO	Polybutylene oxide glycol
PPO	Polyproplene oxide glycol
PTMEG	Polytetramethylene etherglycol
PU	Polyurethane
TDI	Toluene diisocyanate
T_g	Glass transition temperature
SEM	Scanning electron microscopy

Chapter 1

Introduction

1.1 Introduction to Polyurethanes

Historical

Polyurethane (PU) was invented as a fiber-forming polymer by Prof. Otto Bayer in 1937. It was made by reacting an aliphatic 1,8 octane diisocyanate with 1,4 butanediol. The first commercial polyurethane with the trade name Igamid U was made by I.G. Farbenindustrie for artificial fabrics (Bayer, 1937). The early study of polyurethane mainly focused on improving its properties to compete with nylon. Later, the research concentration was turned to the development of PU foams, elastomers and surface coatings (Woods, 1982). In particular, the first PU coating was introduced by Bayer in 1941 (www.bayer.com). And the first polyurethane foam was discovered in 1947, which was followed by the first solid elastomer in 1955. All these polyurethane products developed very quickly to the manufacturing scale. Table 1.1 shows the main historical events of the polyurethane development.

Market Overview

Today, polyurethanes are still highly demanded products. In the 1950s, the world's annual consumption of polyurethane was only 8 million pounds. Up to 1960s, the consumption of polyurethane used in various applications reached 600 million pounds/year (Bruins, 1969). However, from 1996 to 2000, only in the United States,

the demand of polyurethanes had increased from 4,609 to 5,640 million pounds (www.polyurethane.org). The increasing rate was about 6% per year. It was estimated that the world's polyurethane demand was about 16 billion pounds in 1995, which constituted about 5% of the total amount of plastics produced worldwide (Szycher, 1999). The high demand is due to the versatile chemistry of the raw materials used in polyurethane syntheses that make the polymer suitable for a wide range of applications. Table 1.2 summarizes the polyurethane demand in the United States in 1998 by the type of application.

Table 1.1 Historical Events of Polyurethane Development

Year	Event	Reference
1937	I.G. Farbenindustrie applied for the first PU patent	Greman Patent 728,981
1938	First U.S. patent awarded to Rinke et al.	U.S.Patent 2,511,544
1941	First commercial PU coating	www.bayer.com
1947	First PU foam	Woods, 1982
1955	Patent on Estane themoplastic elastomers awarded	U.S.Patent 2,871,218
1971	Patent on polyurethane-silicone elastomer for medical applications	U.S.Patent 3,562,352
1993	Patent on aliphatic biostable polyurethane elastomer	U.S.Patent 5,245,662

Note: Information shown here was obtained from Szycher, 1999.

Table 1.2 Polyurethane Demand by the Type of Application in the United States (1998)

Type	Demand (mm lbs)	Percentage of the Total PU Demand
Flexible Foams	2,222	42%
Rigid Foams	1,382	26%
Coatings	500	9%
Binders	354	7%
Elastomers	207	4%
Adhesives	206	4%
Sealants	146	3%
Others	310	5%
Total	5327	100%

Note: Data shown was obtained from www.polyurethane.org

1.2 Polyurethane Chemistry

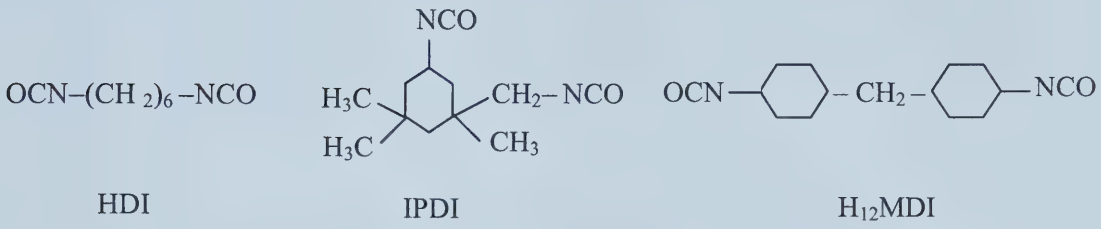
Polyurethanes as we use today actually consist of a wide variety of polymer structures containing the repeating urethane linkages. Basically, polyurethanes are made by reacting diisocyanates with diols as shown in the following equation:

$$O{=}C{=}N{-}R'{-}N{=}C{=}O \; + \; OH{-}R{-}OH \; \rightarrow \; -[-CO{-}NH{-}R'{-}NH{-}CO{-}O{-}R{-}O-]_n-$$

Here, R and R' represent the non-reactive parts of the reactants. Molecules with multiple –NCO and –OH groups could be used to form branched or crosslinked polyurethanes. It is because there are essentially infinite number of choices of R and R', along with the use of multiple functional group reactants, a wide range of physical and mechanical properties can be obtained. For example, if both R and R' contain flexible chain structures with chain lengths of 30-50 carbons, the resultant polyurethane would be fairly elastic. On the other hand, if R and R' contain rigid structures, the resultant polyurethane would be very rigid. Also, one can tailor the final properties of the polymer by adjusting the NCO/OH molar ratio.

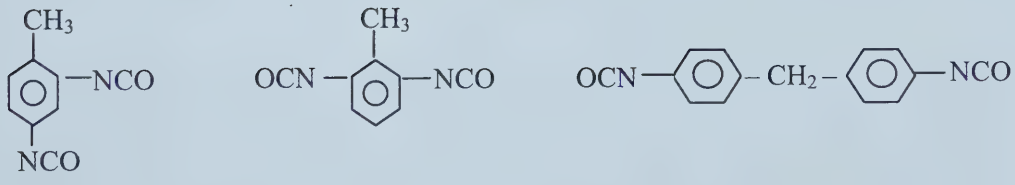
As mentioned above, there are many kinds of raw materials that can be used to synthesize polyurethane. For the isocyanate component, one can choose bi- or polyisocyanates. Polyisocyanates are mainly the adducts or trimers of diisocyanates. They are frequently used because the industrial hygiene requires that the amount of monomeric diisocyanates evaporated to the atmosphere should be minimized. Diisocyanates can be classified into aliphatic and aromatic diisocyanates. Usually, aliphatic diisocyanates are less reactive and slightly more expensive than the aromatic ones. But polyurethanes made from aliphatic diisocyanates are more resistant to hydrolysis, UV light degradation and heat degradation than those from aromatic diisocyanates. These properties make aliphatic polyurethanes more suitable for exterior applications. The most widely used aliphatic diisocyanates are 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and 4, 4'-dicyclohexyl methane diisocyanate (H_{12}MDI). The most commonly used aromatic diisocyanates are toluene

diisocyanate (TDI, 2, 4 and 2, 6 isomers) and 4, 4'-diphenyl methane diisocyanate (MDI). Their chemical structures are shown in Figures 1.1 and 1.2.



HDI IPDI H_{12}MDI

Figure 1.1 Chemical Structures of Commercially Important Aliphatic Diisocyanates



2, 4 – TDI 2, 6 – TDI MDI

Figure 1.2 Chemical Structures of Commercially Important Aromatic Diisocyanates

As for diols or polyols, they can be classified as polyester polyols, polyether polyols and other hydroxyl containing or hydroxyl terminated compounds. Polyester and polyether polyols are most widely used in the polyurethane industry. In general, polyester polyols are used to make elastomers and coatings. Commonly used polyester polyols include poly(ethylene glutarate), poly(ethylene adipate) and poly(ethylene azelate). Their structures are shown in Figure 1.3.

Poly(ethylene glutarate): $HO–[–CH_2CH_2OOC(CH_2)_3COO–]_n–H$

Poly(ethylene adipate): $HO–[–CH_2CH_2OOC(CH_2)_4\ COO–]_n–H$

Poly(ethylene azelate): $HO–[–CH_2CH_2OOC(CH_2)_7COO–]_n–H$

Figure 1.3 Chemical Structures of Commercially Important Polyester Polyols

Polyether polyols are mostly used for flexible or rigid foams, elastomers and sealants. The most important polyether polyols used are: polytetramethylene etherglycol (PTMEG), polyproplene oxide glycol (PPO) and polybutylene oxide glycol (PBO). Their structures are shown in Figure 1.4.

PTMEG: $HO–[–CH_2CH_2CH_2CH_2–O–]_n – H$

PPO: $H–[–O–CH_2–\underset{\displaystyle CH_3}{\underset{|}{CH}}–]_n–OH$

PBO: $H–[–O–CH_2–\underset{\displaystyle CH_2\\ \displaystyle CH_3}{\underset{|\\ |}{CH}}–]_n–OH$

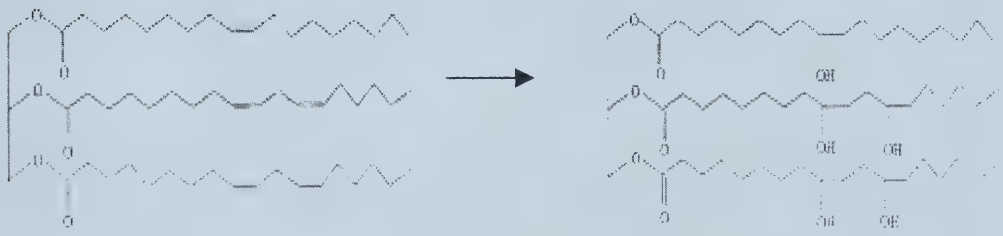
Figure 1.4 Chemical Structures of Commercially Important Polyether Polyols

Almost all commercial polyols currently used for synthesizing polyurethanes are obtained from the petroleum-derived compounds. With oil being an un-renewable resource and much more concern about the environmental protection, the scientific community has become more interested in developing materials that originate from renewable resources, such as agriculture products. This explains why polyols derived from soybean oil (soy-based polyols) have attracted much attention in resent years. In addition, their cost is relatively lower than that of synthetic polyols.

Soybean oil is one type of vegetable oil. Vegetable oils from different sources have different structures, but their skeleton structures are essentially the same. All vegetable oils consist of a triglycreride structure with both saturated and unsaturated fatty acid in the fatty acids long chains. However, the lengths of the three fatty acid chains are different; the number and location of the double bonds also differ. In general, the length of the fatty acid chain varies from 6 carbons (coconut oil, fatty acid

chain: $C_5H_{11}COOH$) to 24 carbons (peanut oil, fatty acid chain: $C_{23}H_{47}COOH$). The length of all three fatty acid chains in palm oil is 16 carbons while that in castor oil is 18 carbons. For soybean oil, the fatty acid chains contain 18 carbons and 5 double bonds (Tan, 1997).

Conversion of various types of vegetable oils into polyols is still a very active research area (Guo, 2000 and Kurth, 2002). However, we focus on soybean polyols in the present work. Figure 1.5 shows the structure of soybean oil and the resulting polyol after full conversion of all double bonds (John et al., 2002):



Soybean oil

Soy-based polyol

Figure 1.5 The Structure of Soybean Oil and the Resulting Polyol after Conversion of all Double Bonds

Generally speaking, the method for converting the soybean oil to soy-based polyol is to epoxide the double bonds on the soybean oil molecules and then open the

epoxided rings (Guo, 2000; Kurth et al., 2002). At present, soy-based polyols have been used for making polyurethane foams and elastomers (Guo, et al., 1999 and John, et al., 2002, Petrovic et al., 2002.) However, such polyols have not been used in synthesizing coatings.

1.3 Polyurethane Coatings

Polyurethane coatings, which generally exhibit excellent abrasion resistance, high adhesion performance, and solvent resistance, are widely used in our daily life and in industrial environments. Compared with coatings made of other film forming polymers, polyurethane coatings have many advantages. First, they have both good decorative and protective performance. The adhesion between polyurethane and various types of substrates, like metals, woods, concretes, plastics, etc., tends to be fairly strong. The elasticity of the material can vary considerably, even to high elongation for leather and fabric substrates. This is a unique property for polyurethane coatings. Other coatings, such as epoxy resins, unsaturated polyester resins, alkyd resins, etc., can only be used as rigid films. The chemical and water resistance of the polyurethane coatings are extremely good. They can resist corrosive chemicals, petroleum products, acid, basic and salt solutions. Hence, they are good for protecting tanks, pipes, equipment commonly used in chemical plants, vehicles, ships and aircrafts. In addition, polyurethane coatings can be used for application in which the environmental temperature can be as low as – 40 °C.

Secondly, the application processes for polyurethane coatings are simple. All conventional methods, like applicator, brush, roller and spray, can be used under

different conditions. The curing temperature range of polyurethane films is also wide. Some films cure at temperatures as high as 180 ºC; others at room temperature or even as low as at 0 ºC (Tan, 1997). The required application process for polyurethane coatings makes it easy to coat on large oil tanks and aircrafts. Also, the types of polyurethane coatings vary from solvent type to 100% solid type and water dispersions for meeting a variety of requirements. According to ASTM standards (Doyle, 1971), the polyurethane coatings can be classified as five categories:

I. Urethane-modified alkyd coatings: This kind of coating is made by the alcoholysis of products of mixtures of oils and isocyanates. The curing process actually involves the oxidation of unsaturated oils.

II. Moisture-cured urethane: This type is cured by atmospheric moisture. In particular, the moisture reacts with the extra isocyanate groups in the prepolymer.

III. Blocked urethane: It is a one-package coating prepolymer with a high level of NCO that is blocked by a certain compounds containing hydroxyl groups (usually phenol). After heating to higher temperatures (about 120 °C ~ 180 °C), the prepolymer was unblocked and give rise to the same reaction as a two-package system.

IV. Prepolymer and catalyst: This is a two-package urethane coating system. One package contains prepolymer made by isocyanates and polyols. The second package contains a separate catalyst to accelerate the reaction and other ingredients to improve flow, bubble release and so on.

V. Two package systems: One component contains diisocyanate adduct while the other polyols.

With all the advantages mentioned, the prices of the polyurethane coatings tend to be higher than those of other coatings. Another drawback is that their application processes are sensitive to the environment (humidity in particular), and their shelf life is rather short. To overcome these disadvantages, intensive research has been carried out to develop cheaper and more stable raw materials.

1.4 Research Objectives

The major thrust of this research is to develop high performance polyurethane coatings made from soy-based polyols. As mentioned, such polyols are inexpensive, abundant, and renewable, especially in Canada. The price of polyols derived from soybean oil is approximately one third of that of most synthetic polyols. Another advantage of the soy-based polyols is that it can be used to make highly crosslinked polyurethane structures because of its three-arm structure.

The first objective of our research was to check if soy-based polyols could be used as film forming materials by reacting them with some selected polyisocyanates under various conditions. As mentioned, the soy-based polyols react with diisocyanates to form foams and elastomers (Guo et al., 2000; John et al., 2002; Petrovic et al., 2002). However, the use of such polyols for coatings applications has not been reported in the open literature.

The second objective is to compare some selected end use properties of the coatings made from soy-based polyols with those made from synthetic ones with comparable properties. Theoretically speaking, soy-based polyols would form highly crosslinked networks that result in tough coatings. However, this is not necessarily the case as urethane reaction may not proceed to completion due to the location of the OH groups. In particular, effects of the NCO/OH molar ratio on the coating performance will be studied.

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www.bayer.com

www.polyurethane.org

Chapter 2

Raw Materials Characterization

2.1 Properties of Raw Materials

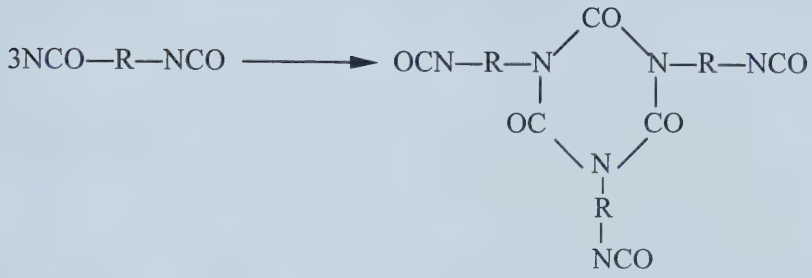
As discussed previously, the raw materials for synthesizing polyurethanes include all components that can react with each other to form the urethane linkage (–NH–CO–O–) in the final polymer. However, only the reactions between diisocyanates (or polyisocyanates) and polyols are of commercial value. For surface coating applications, both aliphatic and aromatic polyisocyanates as well as polyester and polyether polyols can be used. In this Chapter, we will discuss the characteristics of the raw materials used in the present work.

Isocyanates

Isocyanates are highly reactive liquids. They can react with chemical compounds containing hydroxyl groups, such as water, carboxylic groups and amino groups. The invention of isocyanates dates back to the 1800s, when the Germany chemist Wurtz isolated the first isocyanate intermediate. After his work, Hentschel, Curtius, Schroeter, Hoffmann and Lossen further improved the synthetic process. Nonetheless, it was the Bayer Company that played the key role in making isocyanates have commercial value by using them to synthesize polyurethanes (Doyle, 1971).

In our research, the isocyanate component used was a polyisocyanate that exhibits fairly low vapor pressures. This is especially good for coating applications since the amount of polyisocyanates released to the atmosphere would be low.

Polyisocyanates are dimers or trimers of monomeric isocyanates. The preparation of polyisocyanates is by the polymerization of the isocyanates, i.e., self-addition. The reaction is:



The physical properties of the isocyanates and polyisocyanates are very different. In the coating industry, the most commonly used aromatic and aliphatic isocyanates are MDI and HDI (Wicks et al., 1999). Since the isocyanate components we used are polyisocyanates based on MDI and HDI, we only discuss their physical properties here.

The aromatic polyisocyanate we used is a dark brown liquid while the aliphatic one is a clear liquid. Some selected properties of these two types of polyisocyanates are presented in Table 2.1.

Table 2.1 Selected Properties of the Polyisocyanates Used

Property	Aromatic Polyisocyanate	Aliphatic Polyisocyanate
NCO content, %	31.1	23.0
Equivalent wt., avg.	133	183
Viscosity @ 25 °C, mPa·s	150-250	1,100
Specific gravity	1.24 @ 25 °C	1.16@ 20 °C
Flash point	199 °C	158 °C

Note: The data in Table 2.1 was obtained from Bayer.

NCO content, % = mass (g) of NCO per 100 g of polyisocyanate.

Equivalent Weight: the mass (g) of polyisocyanate that gives 1 mole of NCO groups.

Since isocyanates are very reactive and can react with any compounds containing hydrogen, they react not only with alcohol to form urethane linkage but also with water, amine, and carboxylic acids to form amine and urea, respectively. Among all these side reactions, the reaction between isocyanate and water influences the final product properties greatly. The reaction is shown in equation (2.1).

$$R\text{—}NCO + H_2O \longrightarrow \underset{\text{Carbamic Acid}}{[\,R\text{—}NH\text{—}\overset{\overset{O}{\|}}{C}\text{—}O\text{—}H\,]} \longrightarrow \underset{\text{Amine}}{R\text{—}NH_2} + CO_2$$

$$R\text{—}NCO + R\text{—}NH_2 \longrightarrow \underset{\text{Urea}}{R\text{—}NH\text{—}\overset{\overset{O}{\|}}{C}\text{—}NH\text{—}R} \qquad (2.1)$$

These reactions are inevitable in most practical coating application processes because such reaction mixtures can easily be in contact with air which usually contains certain amount of moisture. The carbon dioxide produced by this reaction leads to the bubble formation in the film and the formation of urea that makes the resultant material weaker. Fortunately, polyisocyanates are less reactive with water than monomeric isocyanates. This is why under high humidity conditions, polyisocyanates can still form films without bubbles.

Polyols

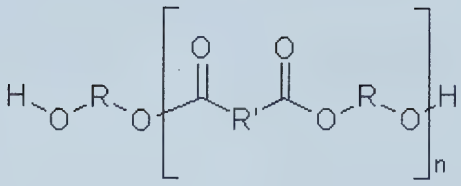
Polyols are the most important raw materials for making commercial polyurethanes. As mentioned in Chapter 1, polyester and polyether polyols are the two principle types of polyols. Polyester polyols were the first hydroxyl-containing materials for making polyurethanes. Most of them are widely used for making coatings, elastomers and fibers. Polyether polyols are more commonly used for preparing flexible and rigid foams. Since the demand of polyurethane foams is much higher than that of other types of products, the consumption of polyether polyols is far higher than the polyester polyols. In this research, since our main objective was to develop high performance urethane coatings based upon soy-based polyols, which contain ester structures, synthetic polyester polyols were used for benchmarking the performance of polyurethane coatings made by soy-based polyols.

Synthetic polyester polyols are prepared by reacting dibasic acid with glycol. There are many kinds of glycols and acids that can be used for such purposes. The most commonly used ones are shown in Table 2.2 (Szycher, 1999):

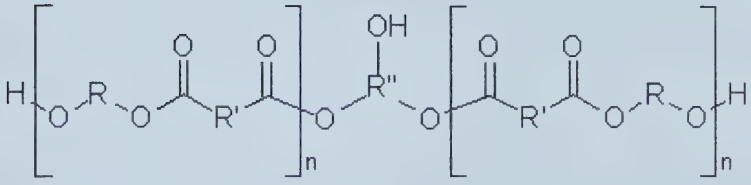
Table 2.2 Important Glycols and Acids for Making Polyester Polyols

Glycol	Acid
1,6 hexanediol	Adipic Acid
Neopentyl Glycol	Azelaic Acid
Butanediol (1,4 & 1,3)	Phthalic Anhydride
Ethylene Glycol & Propylene Glycol	Isophthalic Acid
Cyclohexanedimethanol	Dimethylolpropionic Acid

Two types of synthetic polyester polyols were used and were obtained from Bayer. One contained 2 OH and the other 3 OH groups per molecule. The bi-functional synthetic polyol is an adipate copolymer diol having an equivalent weight of 1,060. The tri-functional one is an adipate copolymer polyol having an equivalent weight of 198. Their structures are shown in Figure 2.1. And some of their physical properties are summarized in Table 2.3.



a. Structure of the Bi-functional Synthetic Polyol



b. Structure of the Tri-functional Synthetic Polyol

Figure 2.1 Structures of the Synthetic Polyols Used

Table 2.3 Selected Properties of the Synthetic Polyols Used

Property	Bi-functional	Tri-functional
Form supplied	Solvent-free liquid	Solvent-free resin of high viscosity
Hydroxyl number (mg KOH / g)	52	280
Equivalent wt., avg.	1,060	198
Viscosity @ 23 °C (mPa·s)	11,000	850 (70% in solvent)*
Specific gravity	1.17	1.18
Water, wt. %	0.1	0.1
Functionality	2.0	3.0

Note: The data in Table 2.3 was obtained from Bayer.

The data with * represents the viscosity after diluted by a solvent.

Hydroxyl number: amount of equivalent KOH (mg) per g of polyol sample.

Equivalent Weight: the mass (g) of polyol that gives 1 mole of OH groups.

As for the soy-based polyols, we chose bi- and tri- functional polyols. Both of them were made from soybean oil. As mentioned in Chapter 1, for making this kind of polyols, the soybean oil is usually epoxided and then the epoxided rings are opened by substance containing hydroxyl groups to obtain the soy-based polyols (Petrovic et al., 2000). But the samples we used were not prepared with such procedures. The samples

were obtained from Urethane Soy System who claimed that a different method was used (Kurth et al., 2002). The new method is related to the transesterification reactions between the vegetable oil (soybean oil) and glycerin/saccharide ester. However, owing to the proprietary nature of the reactions, the details are not known. However, it is expected that the structures of these polyols are similar to those made by the other routes (see Figure 1.5). Note that the soy-based polyols we used contained either two or three instead of five OH groups per molecule as shown in Figure 1.5. Some selected properties of the soy-based polyols used are listed in Table 2.4.

Table 2.4 Selected Properties of the Soy-Based Polyols Used

Property	Bi-functional	Tri-functional
Form supplied	Solvent-free liquid	Solvent-free liquid
Hydroxyl number	53	275
Equivalent wt., avg.	1,058	204
Viscosity @ 23 °C, mPa·s	2,800	2,700
Specific gravity	0.980	0.995
Water, wt. %	0.04	0.04
Functionality	2.0	3.0

Note: The data in Table 2.4 was obtained from Urethane Soy System.

2.2 Structure –Property Relationships of Polyurethane Coatings

The study of coating properties includes every aspect of durability. There exist a wide range of methods that can be used to evaluate and to test coating performance. In our research, the test methods used include adhesion, abrasion and water resistance. These methods were chosen simply because the relevancy to the performance requirements that most coatings need to meet. For example, polyurethane coatings are frequently used as water proofing materials. Therefore, it is important to know their water resistance. In addition to these tests, the glass transition temperatures (T_g) of the materials were also measured utilizing a differential scanning calorimeter (DSC) (Yu et al., 1999; Paolpi et al., 2001; Pielichowski et al., 2001). Knowledge of the glass transition temperature for a coating system is critical for its application because T_g should be outside the temperature range that the coating system will encounter. This will reduce the unnecessary internal stress built up in the system due to frequent thermal transitions. Obviously, T_g is controlled by the types of raw materials and their relative amounts used in the formulation. The processing conditions can also affect the end use properties of the coatings greatly. In the following, we will discuss effects of monomer types and reaction conditions on the film properties to give the reader a source of how various raw materials and their amounts are designed for a coating formulation.

Effects of Monomer Type on Coating Performance

Since there exists a high number of monomers that can be used for polyurethane synthesis, the final properties of polyurethanes vary considerably. First, the structural

difference of the isocyanate component could result in fairly different coating performance. The aromatic ring in the aromatic isocyanates makes the monomers very rigid than the aliphatic ones. So coatings made by aromatic isocyanates have less elasticity and higher T_g than those by aliphatic isocyanates with comparable size. This, in turn, results in differences in their adhesion, abrasion resistance and water resistance. However, quantitative structure–property correlations for the above properties are still lacking. This is somewhat due to the fact that the unpredictability of the reactivity of the NCO groups makes it very difficult to predict the molecular structure of the resultant coating. For example, the presence of the conjugated π electrons on the aromatic rings makes the carbon atom adjacent to NCO group more positive. Therefore, the reaction rate of the aromatic isocyanates is usually a few orders of magnitude higher than that of aliphatic isocyanates (Szycher, 1999). As a result, aromatic isocyanates tend to react with the moisture in the surroundings. This will, in turn, lead to more urea linkages and bubbles formation in the resultant coating.

Secondly, the structural differences between the polyols could also yield different coating properties. Such differences include the polyol type and functionality. For example, the structures of the soy-based and synthetic polyols used in the present work differ significantly. Compared with synthetic polyols, the structure of soy-based polyols allows the formation of well crosslinked coating films. Therefore, the abrasion resistance, adhesion and water resistance should be improved (Chiou et al., 2002). As for how these properties are improved, they have to be determined experimentally. Besides the effects of the polyol types, the functionality of the polyols can also

influence the end use properties. If the functionality of the polyol used is 2, the resultant coating will be more flexible than those made of polyol with a functionality of 3. The increase of polyol's functionality would result in higher abrasion resistance, higher T_g and better water resistance. In addition to the raw material effects discussed above, the process conditions could also influence the final properties greatly.

Effects of Process Conditions on Coating Performance

The different process conditions, such as reaction temperature, the NCO/OH molar ratio and use of catalyst, can affect coating performance. In general, isocyanates react with polyols at room temperature. As mentioned before, isocyanates also react with moisture in air to form CO_2 resulting bubbles in the resultant material. This side reaction occurs relatively easily for aromatic isocyanates with high viscosity. When reaction is carried out at high temperatures (less than 150 °C), allophanate structure would form because the NCO groups could react with the urethane linkages already formed in the coating films to form allophanates (Doyle, 1971). The presence of allophanates alters the material properties. However, such material may be useful for certain applications. Overall, the higher the curing temperature is, the more rigid the polymer film is. At about 250 °C, the decomposition of the polymer begins (Szycher, 1999). In the present work, we carried out all reactions at 60 °C in an oven. In this way, catalyst was not required and most of the curing reactions were completed within a reasonable amount of time.

The NCO/OH molar ratio is a very important parameter that a coating formulator can use to control the end use properties of the coating. Under normal circumstances,

the NCO/OH molar ratio used in practice ranges from 0.9 to 1.1. When the ratio is either too low or too high, it will introduce a great deal of defects to the coating (Petrovic, 2002). Also, the molecular weight of the final polymer will be reduced dramatically; Figure 2.2 shows such dependence.

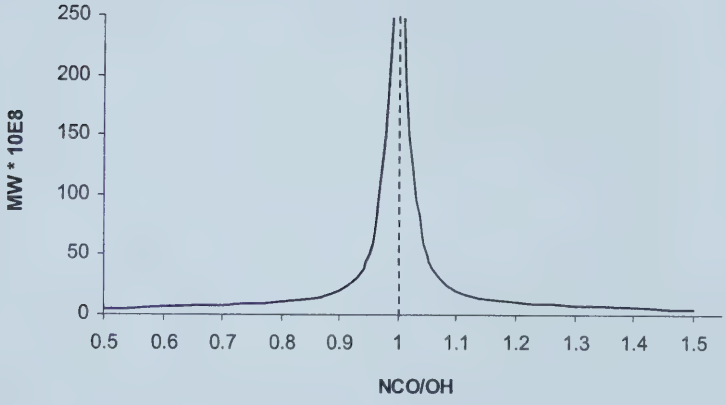


Figure 2.2 The Theoretical Relationship Between Molecular Weight and NCO/OH Molar Ratio (From Szycher, 1999)

As can be seen from Figure 2.2, only when the NCO/OH molar ratio is within the range of 0.9 to 1.1, the molecular weight of polyurethane can reach a useful range (i. e., the polymer exhibits reasonable mechanical strength for practical applications).

The use of catalyst is very common in the synthesis of polyurethane coatings, especially at room temperature. The influence of catalyst is not only on the chemical reaction rate, but also on the final coating properties. The catalysts are mainly

classified into two types: diamine and organic metal compounds. The most commonly used catalysts for polyurethane coatings are diazabicyclo octane (DABCO) and dibutyltin dilaurate (DBTDL). Mixtures of DABCO and DBTDL are also commonly used in industry. Many catalysis mechanisms have been proposed (Wicks, 1999). However, study on the influence of catalyst to coating properties has been scanty. More often, researchers evaluate such effects experimentally. In this research, catalyst was not used since a relatively high reaction temperature was used.

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Chapter 3

Experimental

3.1 Coating Formulations

All raw materials including two polyisocyanates, two synthetic polyols and two soy-based polyols were used as received from Bayer and Urethane Soy Systems. Formulations were developed based on the information depicted in Tables 2.1, 2.3 and 2.4. In particular, the amounts of the reactants were determined using their equivalent weights and the chosen NCO/OH molar ratios. The detailed calculations are shown in Appendix A. A summary of all the formulations developed in this work is given in Table 3.1.

Table 3.1 Summary of Formulations

Symbol	Compositions
Soy-3-ali (1.1)	Soy-based tri-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 1.1/1.0
Syn-3-ali (1.1)	Synthetic tri-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 1.1/1.0
Soy-2-ali (1.1)	Soy-based bi-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 1.1/1.0
Syn-2-ali (1.1)	Synthetic bi-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 1.1/1.0

(Table 3.1 cont'd)

Soy-3-aro (1.1)	Soy-based tri-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 1.1/1.0
Syn-3-aro (1.1)	Synthetic tri-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 1.1/1.0
Soy-2-aro (1.1)	Soy-based bi-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 1.1/1.0
Syn-2-aro (1.1)	Synthetic bi-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 1.1/1.0
Soy-3-ali (1.0)	Soy-based tri-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 1.0/1.0
Syn-3-ali (1.0)	Synthetic tri-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 1.0/1.0
Soy-2-ali (1.0)	Soy-based bi-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 1.0/1.0
Syn-2-ali (1.0)	Synthetic bi-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 1.0/1.0
Soy-3-aro (1.0)	Soy-based tri-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 1.0/1.0
Syn-3-aro (1.0)	Synthetic tri-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 1.0/1.0
Soy-2-aro (1.0)	Soy-based bi-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 1.0/1.0
Syn-2-aro (1.0)	Synthetic bi-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 1.0/1.0
Soy-3-ali (0.9)	Soy-based tri-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 0.9/1.0
Syn-3-ali (0.9)	Synthetic tri-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 0.9/1.0
Soy-2-ali (0.9)	Soy-based bi-functional polyol and aliphatic polyisocyanate,

(Table 3.1 cont'd)

	NCO/OH molar ratio = 0.9/1.0
Syn-2-ali (0.9)	Synthetic bi-functional polyol and aliphatic polyisocyanate, NCO/OH molar ratio = 0.9/1.0
Soy-3-aro (0.9)	Soy-based tri-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 0.9/1.0
Syn-3-aro (0.9)	Synthetic tri-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 0.9/1.0
Soy-2-ali (0.9)	Soy-based bi-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 0.9/1.0
Syn-2-ali (0.9)	Synthetic bi-functional polyol and aromatic polyisocyanate, NCO/OH molar ratio = 0.9/1.0

Abbreviations: Soy — soy based polyols, Syn — synthetic polyols, Ali — aliphatic polyisocyanate, Aro — aromatic aliphatic polyisocyanate, 2 or 3 — the number of functionality. 1.1, 1.0, and 0.9 — the NCO/OH molar ratio. These abbreviations will be used throughout the thesis.

3.2 Preparation of the Coatings

Coatings, based on the formulations shown in Table 3.1, with thickness about 30 mil (i.e., 0.762 mm) were prepared. For each formulation, polyisocyanate and polyol were stirred thoroughly for about 2 minutes in a paper cup to ensure adequate mixing. Then, the mixture was poured on the substrate. In this study, steel panels were used as the substrate. The wet coating film was spread on the panel using a hand-held applicator blade, which can produce films with uniform thickness (ASTM

D 823-95). The surface of the steel panel was pretreated in accordance with ASTM D 2651-01. The wet film was allowed to rest for 20 minutes at room temperature. Finally, the wet film on the steel panel was placed in an oven whose temperature was set at 60 °C. Most of the films took about 15-20 hours to cure completely at such a temperature. Every effort was made to ensure that films were prepared following the same procedure.

3.3 Characterization of the Coating Films

The films prepared according to the procedures described in the previous section were characterized by various testing methods mentioned before. In the following, these testing methods are described.

3.3.1 Adhesion Performance

Obviously, adhesion is a very important characteristic for coating applications. There exist various test methods for measuring adhesion. Among these methods, the pull-off adhesion test is the most widely used one in the coating industry due to its simplicity. The apparatus used is an Elcometer 106 Adhesion Tester, which is shown in Figure 3.1.

Figure 3.1 Elcometer 106 Adhesion Tester

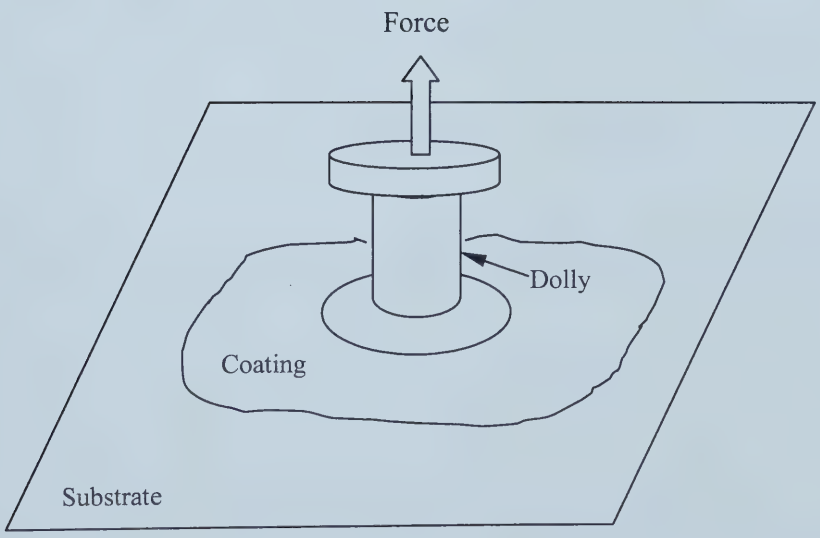

Figure 3.2 Schematic Representation for the Attachment of a Dolly to a Substrate

After all films were cured in oven at 60 °C, they were removed from the oven and naturally cooled to room temperature. The samples were conditioned at room temperature for 24 hours prior to the adhesion test. The first step of the adhesion test was to adhere three dollies to the coating film with extra-strength epoxy adhesive (See Figure 3.2). The adhesive was cured at room temperature for another 24 hours before the dollies were pulled using the Elcometer 106 Adhesion Tester. Procedures described in ASTM D 4541 were followed. The measurement of pull-off force is valid only if the failure happened between the coating film and steel panel. Occasionally, the failure could happen between the dolly and adhesive, or the adhesive and coating film. In these situations, the measured pull-off force was disregarded and the test was repeated. For obtaining accurate results, usually three dollies were used and the average value of the pull-off forces was reported.

3.3.2 Abrasion Resistance

Abrasion resistance is another important property that affects the coating durability. Similar to the adhesion test, there are many methods that can be used. Among such methods, the Taber abrasion testing is probably the best-known and widely used method. The Taber abrasion tester that was used in our studies is shown in Figure 3.3.

Figure 3.3 Taber Abrasion Tester—Abraser 5130

The preparation of the test specimens and testing procedures were carried out in accordance with ASTM D 4060-95. In particular, the coating film with uniform thickness was cured on a standard 100 mm square panel with a 6.3 mm diameter hole in the center of it. The panels were purchased from Taber Industries. For each formulation, test was repeated three times and the average value was reported. The abrasion resistance of a coating is expressed by the weight loss using a certain type of abrading wheel, number of revolutions and specified weight load. In our studies, 200

resolutions with a weight load of 500 g on each side were used. The abrading wheel used was Calibrase CS-17, which is a resilient wheel for testing normal organic coating films.

3.3.3 Water Resistance

Water is considered to be a deteriorating agent to most organic coating films. To quantify the water resistance of a coating film, water absorbance is often measured. In the present work, the water immersion method was used to test the amount of water absorbed as a function of immersion time. The preparation procedures of coating films for this test were the same as mentioned in Section 3.2. A dry film sample was weighted and immersed in a beaker filled with distilled water at room temperature. After soaked for a certain time, such as 5 hours, 10 hours, etc., the film was taken out and wiped by paper towel to eliminate water on the film surface. Then, it was weighed immediately. The test was continued until the weight of the film did not change. The water absorbance then can be calculated and the time dependence of water absorbance can be obtained. The test procedures used were in accordance with ASTM D870-97.

3.3.4 Glass Transition Temperature

The glass transition temperature (T_g) is a useful parameter to determine the temperature range that a coating system can be used. Like many other physical properties, T_g can also be measured by various methods. In this work, differential scanning calorimetry (DSC) was used. The equipment used was DSC model 2910 made by T.A. Instruments. The specimens were prepared as described earlier. The testing procedures were in accordance with ASTM D 3418-99. The mass of sample

used for each run was about 10-20 mg and the temperature range used was from –100 to 250 °C at a heating rate of 20 °C / min under a nitrogen atmosphere.

3.3.5 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy analysis was used to investigate the structural difference for the polyurethane made by different formulations. The FTIR spectra were conducted on a Nicolet Magna – IR 750 spectrometer with a resolution of $2cm^{-1}$. The samples were made by cutting the films, which were prepared as reported previously, into small, thin pieces and flattened with KBr. For each sample, the scan was carried out from a wave number of 4000 to 500 cm^{-1} and 128 scans were averaged to determine the intensity of the peaks. The wave number regions observed in this study focused on the N—H region (1600—1800 cm^{-1}), the amide I region (3200—3500 cm^{-1}) and –NCO region (2200—2300 cm^{-1}).

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Chapter 4

Results and Discussion

4.1 Quality of Films

Not all polymers can form films. This is simply because some polymers possess fairly high surface tensions that prevent them from forming films. The film formation process is not a well understood but very important process that affects the quality and performance of thin film coatings. Since all the coatings we developed in this project were solvent free, the important factors that affect the film formation process are the surface tensions of the monomers and oligomers used, their crosslinking reactions (Duskova-Smrckova M, 2002) and the mixing temperature. Except the mixing temperature, the first two factors are significantly influenced by the types of raw materials and the NCO/OH molar ratio used in a particular formulation. Different formulations give rise to different crosslinking structures.

In the following, the difference of film appearance of the formulations described in Table 3.1 will be discussed, followed by the corresponding performance. Since the film appearance was observed by naked eyes, the discussion tends to be qualitative in nature. Also, subtle differences between the appearances of the films may not be captured. Table 4.1 only shows the appearances of the films made by 8 formulations that represent the reactions at equal NCO/OH molar ratio. As for the formulations at the other molar ratios, the appearances of the films are not shown here because the

differences between the appearances of these films are similar to what are shown in Table 4.1.

Table 4.1 Appearances of Selected Films (NCO/OH Molar Ratio = 1.0/1.0)

Formulation	Film Appearance Description
1. Soy-3-Ali	Shiny, smooth, continuous, hard film, no bubbles and dents.
2. Syn-3-Ali	Shiny, smooth, uneven shrinkage, hard film, some bubbles.
3. Soy-2-Ali	Shiny, smooth, continuous, hard film, no bubbles.
4. Syn-2-Ali	Shiny, smooth, shrinkage, elastic film, some bubbles.
5. Soy-3-Aro	Shiny, smooth, continuous, hard film, bubbles and dents.
6.Syn-3-Aro	Not shiny, rough, uneven shrinkage, hard film, a lot of bubbles and dents.
7. Soy-2-Aro	Shiny, smooth, continuous, hard film, bubbles and dents.
8. Syn-2-Aro	Shiny, smooth, shrinkage, elastic film, bubbles and dents.

When aliphatic polyisocyanate was used, it was observed that films formed by soy-based polyols (formulations 1 and 3) possessed fewer defects than those by synthetic polyols (formulations 2 and 4). In particular, formulations using soy-based polyols exhibited no bubbles while this is not the case for synthetic polyols. This is because the viscosity of the synthetic polyols is much higher than that of the soy-based polyols (see Chapter 2). When the raw materials were mixed, air was naturally brought into the mixture in the form of bubbles. The higher the viscosity of the mixture, the more difficult it is for such bubbles to escape. It is note worthy that the bubbles observed were not caused by the side reaction between isocyanates and moisture present in the air. If the bubbles were formed because of the side reaction, more bubbles would have been observed at a lower curing temperature. This is because when room temperature is used, the chance of having the side reaction increases as the materials take about 7-10 days to cure completely. Obviously, the presence of air bubbles can lead to the concentration of stresses when the film is subjected to external stress and could result in poor mechanical properties (Wicks, 1999).

Another major difference between the above two groups of formulations is the film shrinkage problem. Formulations 1 and 3 exhibited no shrinkage while formulations 2 and 4 significant shrinkage. But the shrinkage is obvious for the synthetic polyols. The film shrinkage is mainly attributed to the volume decrease as a result of the curing reaction. This is simply because free volume of polymers is

generally lower than that of monomers. The current results suggested that the free volume of soy-based polyols and that of the corresponding polymer are comparable. Usually, the consequence of volume change is that stress could build up within the coating, especially on a rigid surface (Lange et al., 1997). Therefore, the shrinkage could result in considerable cracking during the lifetime of coating.

As shown in Table 4.1, almost all formulations yielded hard films except formulations 4 and 8 for which synthetic bi-functional polyols were used. These results are reasonable because among all the polyols used, the bi-functional synthetic polyol contained a fairly flexible linear structure resulting in elastic films.

Compared the films formed by aromatic with those by aliphatic polyisocyanates, the major difference is that aromatic polyisocyanates tend to form films with bubbles and dents. The bubbles are likely to be attributed to the higher curing rates of aromatic isocyanates. In general, the film appearance of the formulations using aromatic polyisocyanates is not as good as that of the aliphatic one. However, the films formed by aromatic polyisocyanate exhibited similar trends on the other aspects of the film appearance.

4.2 Adhesion Performance

In general, whether good adhesion could be achieved between a coating system and a specific substrate depends on three factors: wetting, diffusion and mechanical interlocking (Hartshorn, 1986). In the present work, wetting is the factor that controls the adhesion of the coating systems of interest since different combinations of the raw

materials (i.e., different formulations) result in differences in their surface wetting abilities. The diffusion is not significant in the current systems since it is believed that there exists almost no diffusion of the polymer molecules into the substrate used. The mechanical interlocking, which represents the effect of surface roughness on adhesion property, could also be neglected in the current studies because the substrates we used in all experiments were treated in the same manner. As a result, any differences observed in the adhesion for the formulations would be very likely due to their surface wetting behavior.

In general, surface wetting is mainly influenced by surface tension. Surface tension is the force that minimizes the surface area of a liquid when it is in contact with other fluids or liquids. Therefore, coating materials with low surface tensions would exhibit better wetting performance on the substrate. The surface tension of a liquid is mainly characterized by its contact angle (Hartshorn, 1986). But in two-component coating systems, like the ones we studied here, the contact angle is difficult to measure by conventional experimental methods (Yekta - Fard et al., 1992). This is because the curing reaction between diisocyanates and polyols starts immediately after they are mixed. The properties of mixture keep changing until it forms a solid film. This means that it is practically impossible to predict adhesion performance of two-component polyurethane coatings simply based on the individual component physical properties. As a result, all the adhesion is characterized by adhesion test on the resultant solid films. Here, we carried out such measurements according to the pertinent ASTM standard, which was described in Chapter 3. The corresponding results for the

formulations are shown in Table 4.2 and Figure 4.1. Here, Table 4.2 summarizes the results for the formulations prepared by tri-functional polyols at different NCO/OH molar ratios, while Figure 4.1 is for bi-functional polyols.

As can be seen in Table 4.2, the magnitudes of the pull-off force are greater than 500 psi, which is considered to be fairly high for coating purposes.

Table 4.2 Adhesion of Coatings with the Use of Tri-functional Polyols at Different NCO/OH Molar Ratios

Formulations	soy-3-ali	syn-3-ali	soy-3-aro	syn-3-aro
Pull-off force (psi)	>500	>500	>500	>500

Note: For each formulation, the NCO/OH molar ratio includes:

1.1:1, 1.0:1 and 0.9:1.

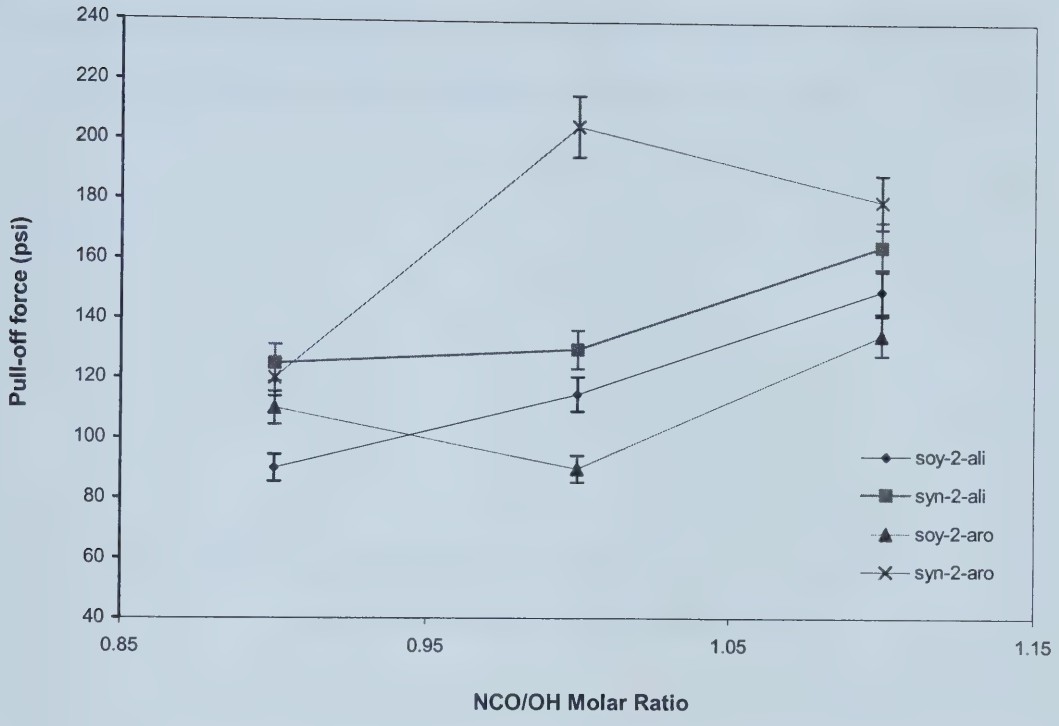


Figure 4.1 Adhesion—NCO/OH Molar Ratio Relationship for Coatings Synthesized Using Bi-functional Polyols

From the data shown in Table 4.2 and Figure 4.1, it is obvious that the adhesion strength of coatings made by tri-functional polyols is much stronger than that of the films made by bi-functional polyols. The observation is very likely attributed to the difference in the surface wetting characteristics of the raw materials used. For tri-functional polyols, the hydroxyl number is around 280, while that of the bi-functional polyols is only about 52 (these data were given in Chapter 2.). As a result, the tri-

functional polyols contain a lot more polar functional groups than the bi-functional polyols. This lead to good wetting on the steel surface since steel surfaces are normally covered with a monolayer hydroxyl groups (Mittal, 1983; Reinhard, 1987) as shown in Figure 4.2, which is easy to form interaction with polar functional groups.

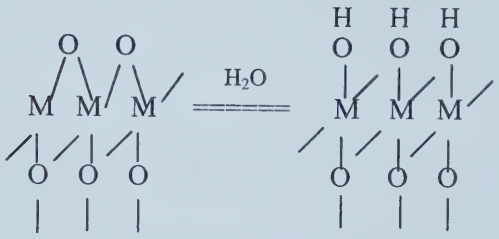


Figure 4.2 Schematic Illustration of Water and Oxide Layers on Metal Surface (From Mittal, 1983)

With the progress of the curing reaction, the interaction at the interface continued to be promoted by the formation of more hydrogen bonds. In particular, the hydrogen bonds at the interface were formed by hydroxyl groups from the polyols and the amine groups from the urethane groups (-NH-CO-O-) in the polymer chains (Wicks, 1999). Since tri-functional polyols contain more hydroxyl groups than bi-functional polyols, they can form more urethane groups (-NH-CO-O-) in the final polymer film, which, in turn, enhances the adhesion.

It can be seen from Figure 4.1 that the adhesion for the films made by bi-functional polyols increased with increasing of NCO/OH molar ratio. This trend is

reasonable because more chemical bonds could be formed between the coating materials and the substrate. The presence of covalent bonds between polymer molecules and the substrate has been shown by some researchers (Wu, 1982; Mitta, 1983; Hartshorn, 1986 and Wicks, 1999). In the present case, the isocyanate component could form chemical bonds with the hydroxyl groups on the substrate surface to give rise to covalent urethane linkages. Similar reaction was observed on the wood surface (Rowell et al., 1981). However, the number of hydroxyl groups on steel surfaces should be less than that of wood surfaces.

Another note worthy point in Figure 4.1 is that films made by synthetic polyols showed better (on average) adhesion. This may due to the elastic natures of those films. Since elastic films can absorb energy when subjected to pull-off stress. Consequently, the total pull-off force exerted on the elastic films could be higher than that on the hard films even though the actual pull-off force (adhesion force) for separating the coating and substrate may the same.

Based on the foregoing discussion, it was concluded that the adhesion strength is very good for all films made with the use of tri-functional polyols, regardless of the type. On the other hand, the use of bi-functional polyols did not yield films exhibiting strong adhesion.

4.3 Abrasion Resistance

As mentioned in Chapter 2, high abrasion resistance is required for certain coating applications. In general, polyurethane exhibits fairly high abrasion resistance

(Palsule, 1991) due to the strong urethane covalent bonds and the associated intermolecular hydrogen bonding. Acyclic or cyclic intermolecular hydrogen bonds can be formed between polyurethane chains (Figure 4.3).

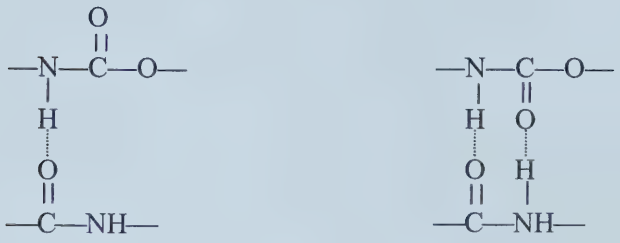


Figure 4.3 Intermolecular Hydrogen Bonds (From Wicks, 1999)

According to Wicks (1999), the reversible dissociation and formation of hydrogen bonds make polyurethane coatings have high abrasion resistance. When external stress exerted on the materials, hydrogen bonds could absorb a significant amount of energy by dissociating themselves allowing more intermolecular space for the adoption of more molecular conformations without breaking the chemical bonds. After the stress is removed, hydrogen bonds reform. Recent experimental results of Petrovic (2002) on polyurethane synthesized with the use of monomeric MDI and soy-based polyols support such a theory.

In this work, the abrasion resistance of the films shown in Table 3.1 was also investigated. The test method was described in Chapter 3 and the experimental results are shown in Figures 4.4 and 4.5.

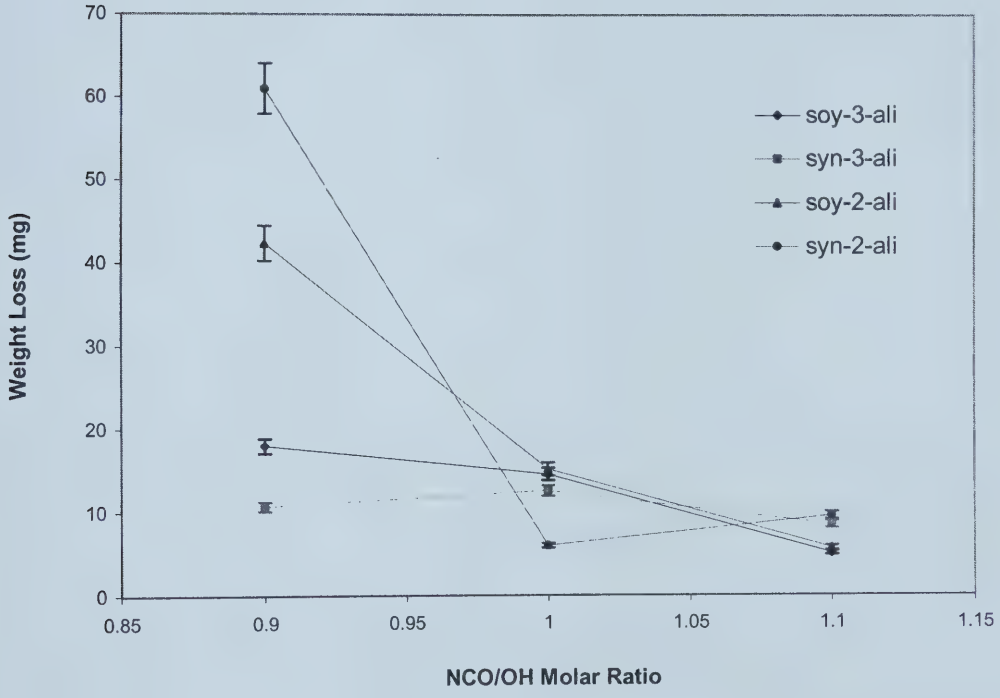


Figure 4.4 The Effect of NCO/OH Molar Ratio on Abrasion Resistance (Aliphatic Polyisocyanate)

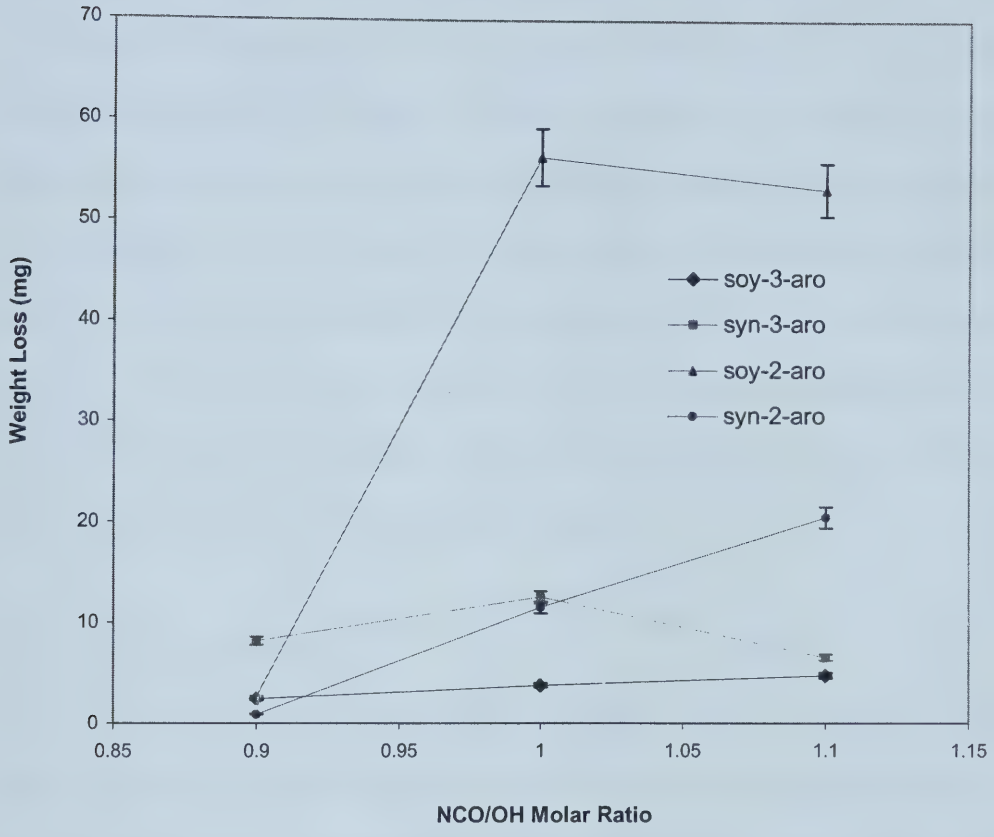


Figure 4.5 The Effect of NCO/OH Molar Ratio on Abrasion Resistance (Aromatic Polyisocyanates)

Figure 4.4 illustrates the NCO/OH molar ratio dependence of abrasion resistance for the aliphatic polyurethane coatings. It was observed that when the NCO/OH molar ratio increased, the weight loss decreased, indicating that better abrasion resistance was achieved. The observed trend conforms to the theory proposed by Wicks. When the NCO/OH molar ratio increased, the crosslinking density of polyurethanes increased. It

is also evident that films by tri-functional polyols exhibited better abrasion resistance than the films made by bi-functional polyols, especially at low NCO/OH molar ratios.

However, the results for the aromatic polyurethanes (Figure 4.5) are rather different from those shown in Figure 4.4. In fact, the results are in contradiction to the foregoing discussed theory. First of all, the weigh loss seemed to be rather insensitive to the NCO/OH molar ratio except the samples made of bi-functional soy-polyols. Such observation is very likely due to the fact that the isocyanate component used was polymeric MDI (a trimer of monomeric MDI). This is because the isocyanate groups in such a polyisocyanate would experience considerable steric hindrance. As a result, this could decrease the chance of the crosslinking reaction.

4.4 Water Absorbance

Polyurethane possesses strong polarity and forms hydrogen bonding (Szycher, 1999). As a result, it has the tendency to absorb water. Due to the hydrophobicity of vegetable oil polyols, polyurethane synthesized from this type of polyol tends to be more hydrophobic than the conventional polyurethanes. Here, we tested the hydrophobicity of selected formulations using the water immersion method, which was described in Chapter 3. The test results for aliphatic and aromatic polyurethane coatings at a NCO/OH molar ratio of 1.1/1.0 are shown in Figure 4.6 and Figure 4.7, respectively. As for the results at other molar ratios, they exhibited fairly similar trends.

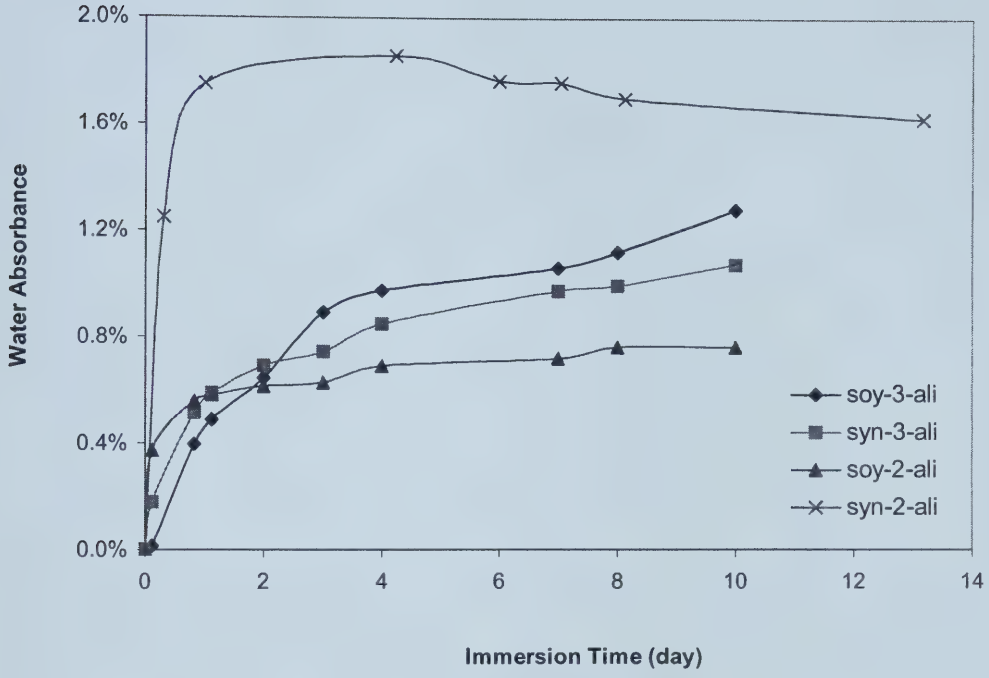


Figure 4.6 Water Absorbance Curves (Aliphatic PU; NCO/OH = 1.1/1.0)

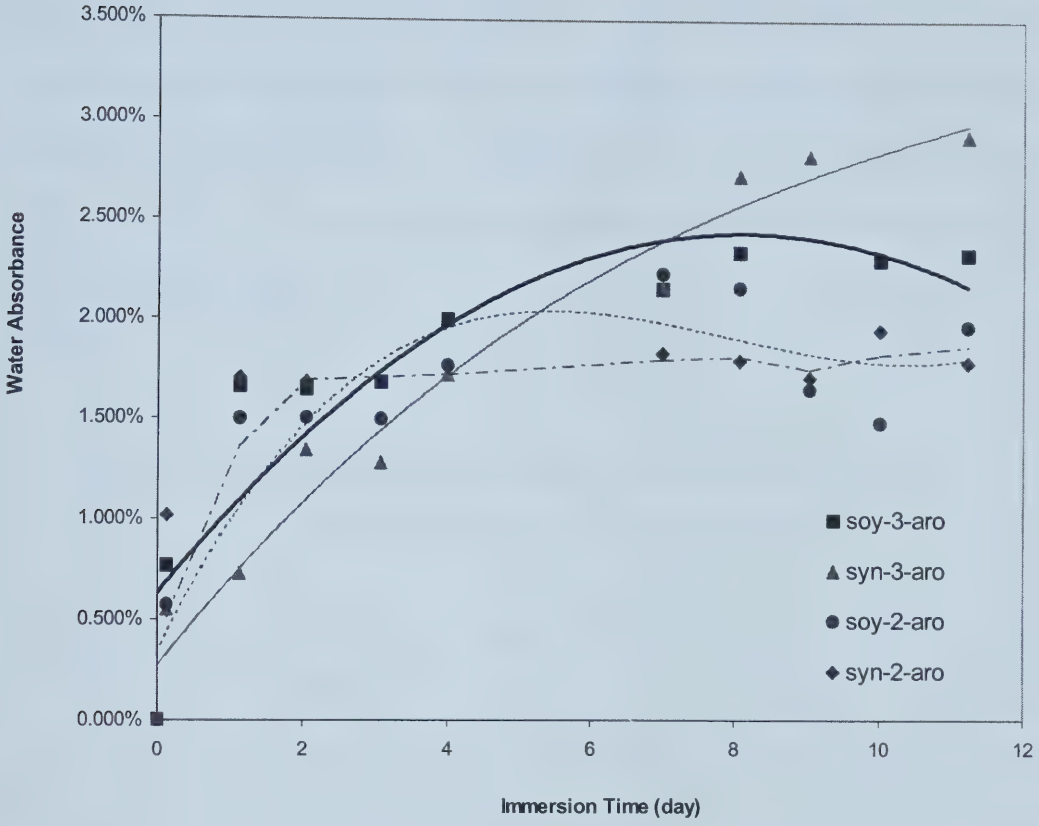


Figure 4.7 Water Absorbance Curves (Aromatic PU; NCO/OH = 1.1/1.0)

As can be seen from Figure 4.6, the water absorption rate was fairly high in the first couple days and started to level off after 3 days. It seems that the difference between soy-based and synthetic polyurethanes is small (the largest difference is less than 1.2%). Nevertheless, since the highest water absorbance is about 1.8%, the water resistance of these films is considered to be good for most coating applications.

Although the shape of the water absorbance curves for the aromatic polyurethanes are similar to that of Figure 4.6, the values are slightly higher. The highest value of water absorbance is about 3%, indicating that water resistance of these films is not as good as those made by aliphatic polyisocyanate. Such trend is clearly shown in Table 4.3. Here, data for the formulations with the NCO/OH molar ratio of 0.9/1.0 are also included.

Table 4.3 Maximum Water Absorbance of Formulations Described in Table 4.1 (NCO/OH = 1.1/1.0 and 0.9/1.0)

NCO/OH	Soy-3-Ali	Syn-3-Ali	Soy-2-Ali	Syn-2-Ali	Soy-3-Aro	Syn-3-Aro	Soy-2-Aro	Syn-2-Aro
1.1/1.0	1.28%	1.08%	0.76%	1.86%	2.33%	2.92%	2.23%	1.94%
0.9/1.0	2.51%	2.47%	1.69%	2.13%	3.56%	4.64%	3.31%	2.44%

As can be seen from Table 4.3, when the NCO/OH molar ratio increased, the maximum water absorption decreased, indicating that the extent of film swelling decreased. In general, the extent of the swelling of a crosslinked film in a solvent is used to determine its crosslinking density. The higher the degree of crosslinking is, the lower the extent of swelling is (Hill, 1992). The same principle applies when the solvent used is water. However, the degree of swelling of a coating film in water tends to be low compared to the use of other organic solvents, the data is seldom used to

calculate the crosslinking density. Nonetheless, water absorbance can still be used to infer crosslinking density qualitatively. According to the present results, the crosslinking density of the polyurethane seems to decrease with decreasing of NCO/OH molar ratio.

In addition to the effect of the NCO/OH molar ratio on the maximum water absorbance, the isocyanate component can also influence the maximum water absorbance. As shown in Table 4.3, the maximum water absorbance of the films made by aromatic polyisocyanate is higher than that of the films made by aliphatic polyisocyanate, indicating that the crosslinking density of the former materials is lower. This is probably attributed to the large steric hindrance in the aromatic polyisocyanate.

In summary, the water resistance of all films is adequate for coating applications. However, the films made by aliphatic polyisocyanate showed better water resistance. At higher NCO/OH molar ratio (1.1/1.0), the water resistance of the films was better. Nonetheless, data suggested that both soy-based and synthetic polyols yielded polyurethane with similar water resistance.

4.5 Glass Transition Temperatures of the Coatings

In general, the glass transition temperature (T_g) of a polymeric material is an important parameter that determines the type of its application. The T_gs of crosslinked polyurethane coating films are affected by several factors. These include the relative amounts of the soft (polyols) and hard (polyisocyanates) segments, the crosslinking

density and the amount of hydrogen bonding. T_g can be measured by a variety of methods. And different methods yield different T_g values (usually within a few degrees range). In this study, we used differential scanning calorimetry (DSC) to obtain T_gs of the polyurethane films. The test method was described in Chapter 3. Measurements were carried out on the formulations described in Table 3.1. The formulations exhibited a wide range of T_g from – 44 °C to 86 °C. In order to adjust the T_g of a coating system, one could use a mixture of polyols in the formulation.

4.5.1. Glass Transition Temperatures (Aliphatic Polyisocyanate + Various Polyols)

The DSC curves for aliphatic polyurethane films at different NCO/OH molar ratios are shown in Figures 4.8, 4.9, 4.10 and 4.11. In these figures, the arrows indicate the locations of T_g.

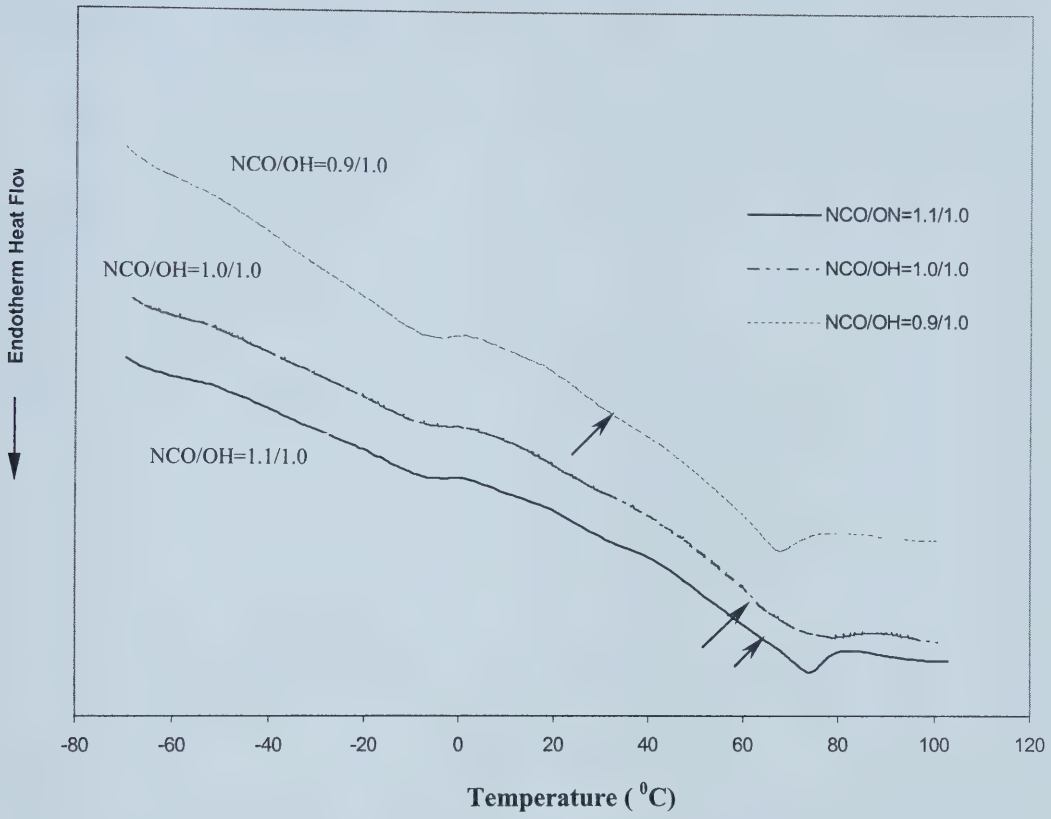


Figure 4.8 DSC Curves for Soy-3-Ali Films at Different NCO/OH Molar Ratios

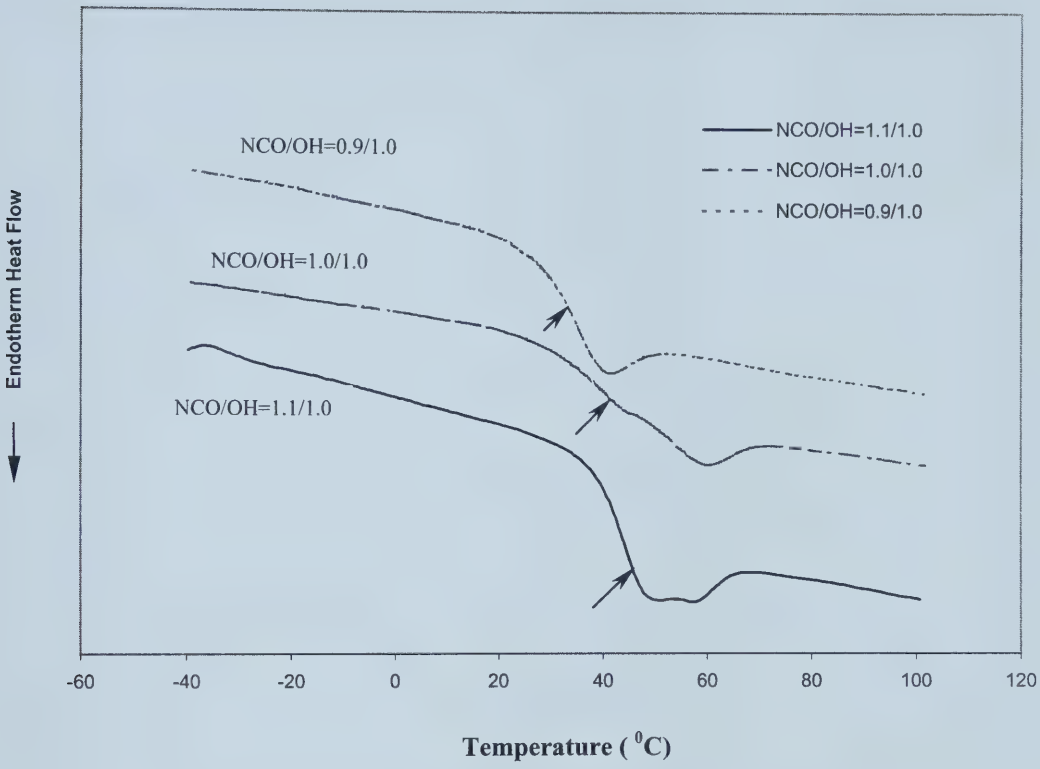


Figure 4.9 DSC Curves for Syn-3-Ali Films at Different NCO/OH Molar Ratios

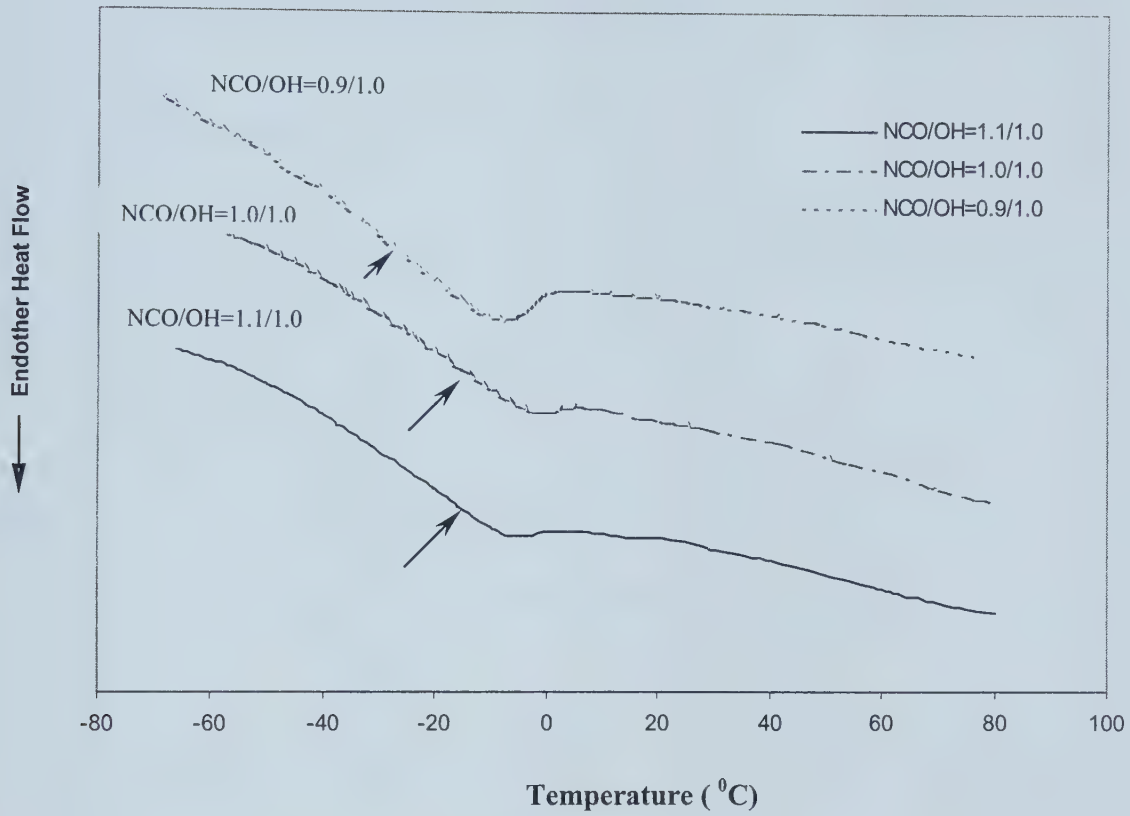


Figure 4.10 DSC Curves for Soy-2-Ali Films at Different NCO/OH Molar Ratios

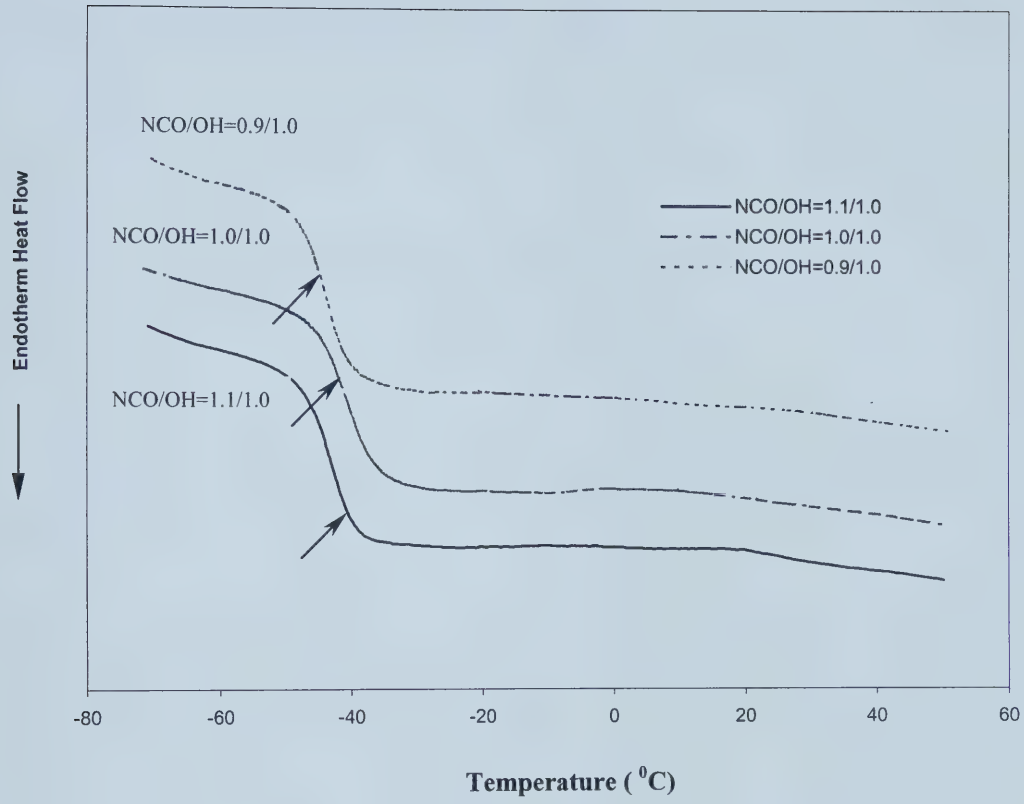


Figure 4.11 DSC Curves for Syn-2-Ali Films at Different NCO/OH Molar Ratios

As can be seen from all the above figures, the position of T_g was affected by the NCO/OH molar ratio. The T_g values, which were determined based on the DSC curves, are summarized in Table 4.4. To identify the T_g for each DSC curve, two

tangent lines were drawn on the parts of the curve before and after the thermal transition, and T_g was determined as the temperature in the middle of the temperatures corresponding to the tangent points (see Figure 4.12).

Table 4.4 T_g of the Polyurethane Coatings at Different NCO/OH Molar Ratios

NCO/OH Molar Ratio	Tg for Soy-3-Ali	Tg for Syn-3-Ali	Tg for Soy-2-Ali	Tg for Syn-2-Ali
1.1/1.0	71	44	-17	-41
1.0/1.0	61	39	-12	-41
0.9/1.0	23	35	-32	-43

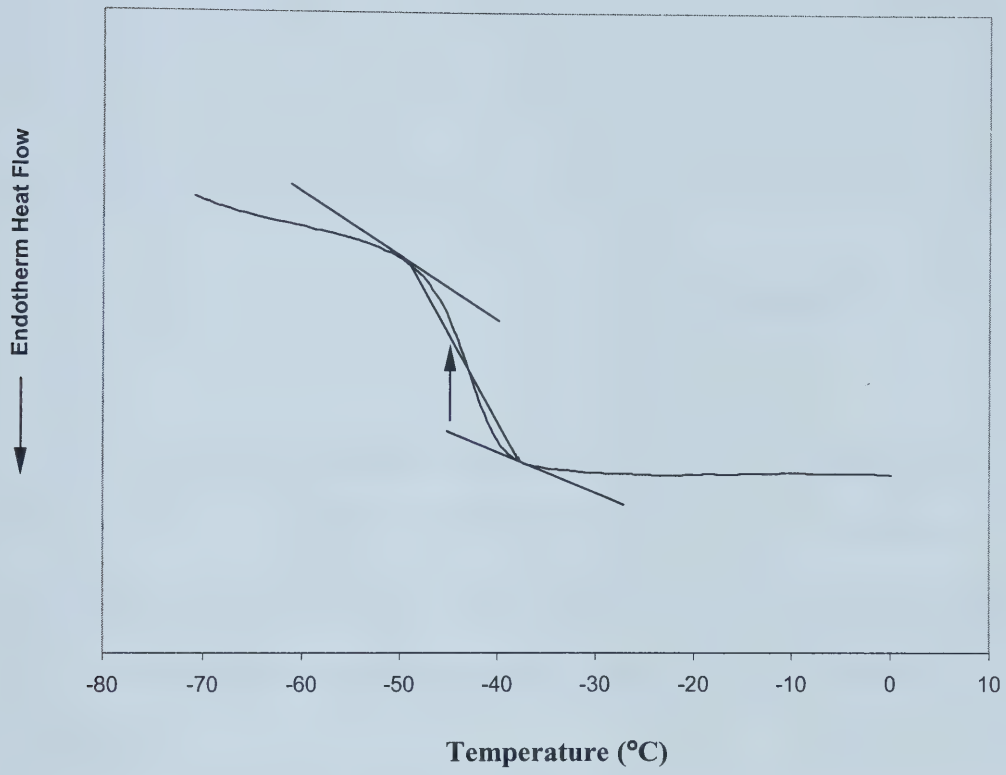
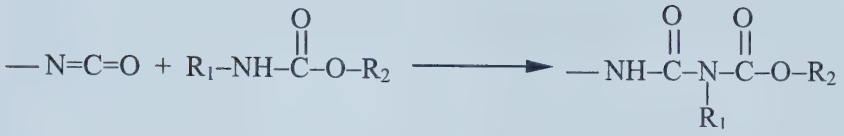


Figure 4.12 Schematic Representation for the Determination of T_g

As indicated in Table 4.4, the glass transition temperature increased with increasing NCO/OH molar ratio. This trend is consistent with what has been reported in literature (Petrovic et al., 2002; Chiou et al., 2002). At higher NCO/OH molar ratio (1.1/1.0), the excess –NCO groups could continue to react with the existing urethane

groups to form 3-dimensional allophanate (Doyle, 1971). The reaction is shown by equation (4.1).



(4.1)

Allophanate

The formation of allophanate would give rise to more crosslinked structures within the resultant coating films, which exhibit a high glass transition temperature. On the other hand, when the NCO/OH molar ratio was low, the excess –OH groups may act like plasticizers within the resultant polymer (Petrovic, 2002). As a result, the T_g is decreased.

Compared the T_gs of the films made by tri-functional soy-based polyol with tri-functional synthetic polyol, it was observed that the former films showed higher T_gs than the latter. The only exception is in the case where lower NCO/OH molar ratio (i.e., 0.9/1.0) was used. In general, differences in T_gs are mainly due to the influence of chemical structure (polymer backbone flexibility), crosslinking density and the effect of dangling chains. The following explains how these factors affect the T_g of polyurethane.

At the exact stoichiometry (NCO/OH=1.0/1.0), there are no excess –NCO and –OH groups. As a result, the T_g of the polymer is mainly controlled by the rigidity of its backbone structure and the crosslinking density. The backbone structure of polyurethane made by soy-based polyol (triglycerides) is usually more rigid than that of synthetic polyol. In terms of the crosslinking densities of the polymers, one can evaluate them by comparing their corresponding molecular weight between crosslinks (M_c). Here, M_c can be calculated using the following equation (Zlatanic et al, 2002).

$$M_c == \frac{M\,(\text{polyol}) + (f/2)\,M\,(\text{polyisocyanate})}{f/2} \qquad (4.2)$$

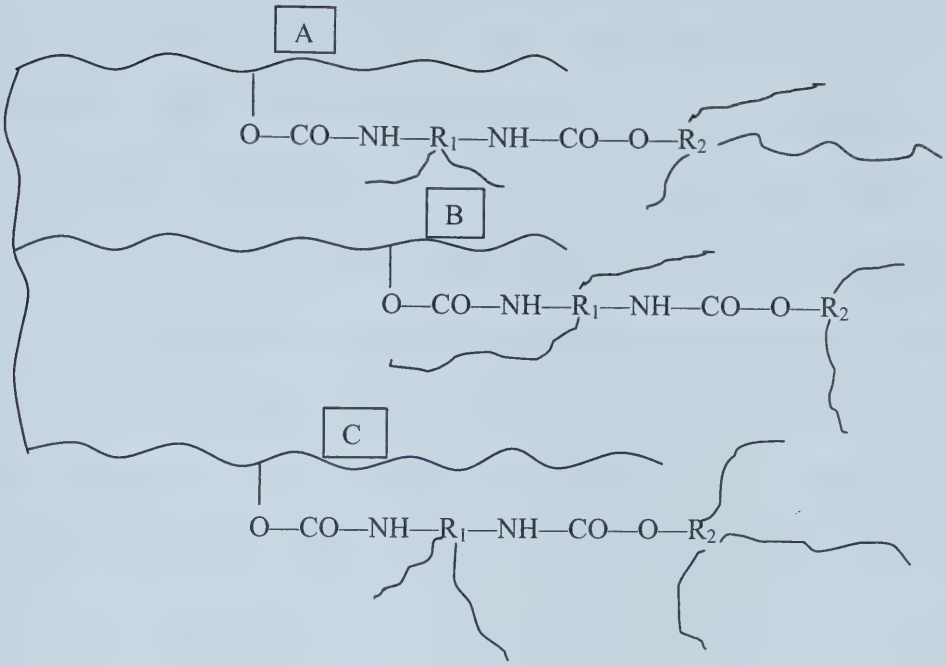
where, M (polyol) and M (polyisocyanate) are the equivalent weights of the polyol and polyisocyanate used in the curing reaction; f is the number of functionality of the polyol used.

Here, the above equation is only suitable for determining M_c for tri-functional polyols and polyisocyanates under the conditions of full conversion and no intermolecular reactions of the functional groups on the same molecule. Assuming that the structure formed by the tri-functional monomers used in the present work can be described by the above equation and the equivalent weights of the polyols were almost comparable (i.e. E.W. of the tri-functional soy-based polyol = 204 and that of the synthetic polyol = 198), the corresponding M_c values for tri-functional soy-based and synthetic polyol are 774 and 762, respectively. Since the difference of M_c is not

statistically significant, it was concluded that both types of polyols yielded structure with similar crosslinking density. This result suggested that the observed higher T_g of the soy-based polyurethane is mainly due to the difference in the backbone flexibility. This may also be the reason for the aliphatic polyurethane made from soy-based polyol.

At higher molar ratios (e.g. NCO/OH=1.1/1.0), excess –NCO groups can continue to react with urethane groups [equation (4.1)]. Since urethane groups had already existed in the polymer backbones, the reaction of equation (4.1) increased the backbone rigidity further. As a result, the T_g of the film made by tri-functional soy-based polyol should be higher than that of tri-functional synthetic polyol, as observed in the present data.

When the NCO/OH molar ratio is low (e.g. 0.9/1.0), excess –OH groups might act as plasticizers to lower its T_g. Under this situation, T_g is mainly determined by the flexibility of polymer backbone structure and plasticization effect of the dangling chains. Here, dangling chains refer to the parts of the molecules that do not belong to the crosslink network as shown in Figure 4.13. Actually, the T_g of the polymer made by tri-functional soy-based polyol is a balance of backbone rigidity and dangling chain flexibility. The observed decrease in T_g value was probably caused by the high dangling chain flexibility of the polyol used. As for the films made by bi-functional polyols, same explanation may apply.



Note: A, B and C are dangling chains.

Figure 4.13 Schematic Illustration of Dangling Chains

4.5.2 Glass Transition Temperatures (Aromatic Polyisocyanate + Various Polyols

In this section, the test samples used were almost the same as those in Section 4.5.1, except that isocyanate component used was aromatic polyisocyanate. The main differences of T_gs were caused by the structural difference of these two polyisocyanates. The principle difference of their structures is the presence of two

aromatic rings (phenyl groups) in aromatic polyisocyanates. In general, aromatic rings are fairly rigid chemical structures and present certain steric hindrance for the polymerization reaction. The rigid chemical structure would lead to an increase in T_g, but steric hindrance would decrease the degree of crosslinking, which lead to a decrease in T_g. The final T_g is simply a balance of the two factors. As mentioned previously, DSC was used to determine the T_gs. Since the resultant DSC curves for the aromatic polyurethanes are very similar to those for the aliphatic ones, they are presented in Appendix B, rather than here. However, we present the NCO/OH molar ratio dependence on T_g here in Figure 4.14. For comparison purpose, data shown in Table 4.4 are presented in Figure 4.15.

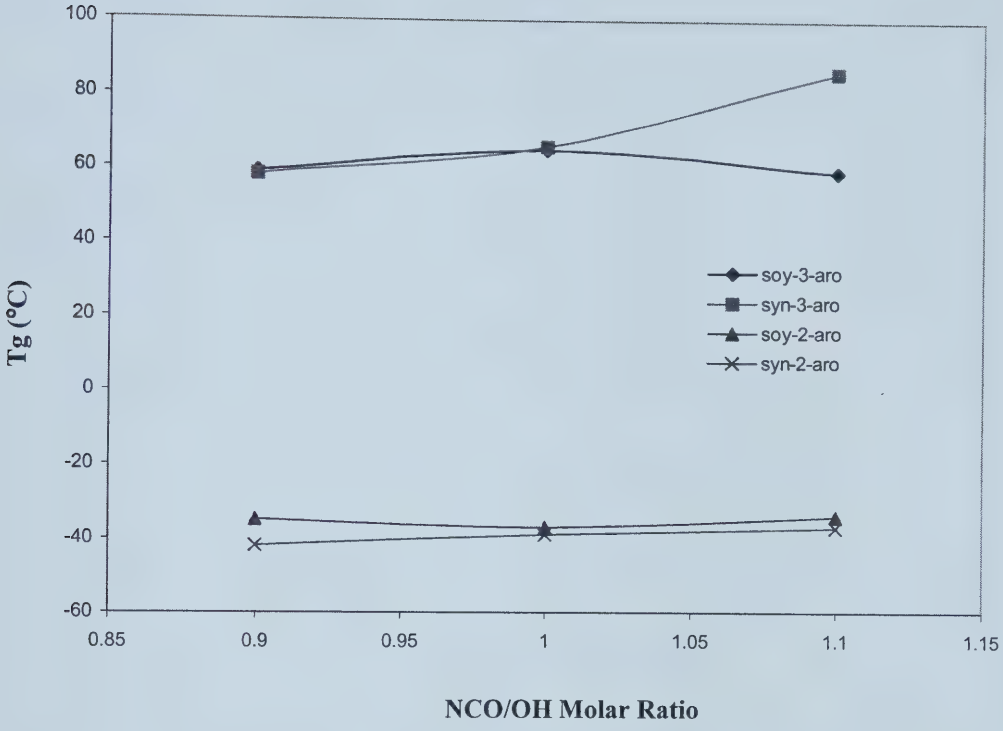


Figure 4.14 The Effect of Molar Ratio on T_g for the Aromatic Polyisocyanate Formulations

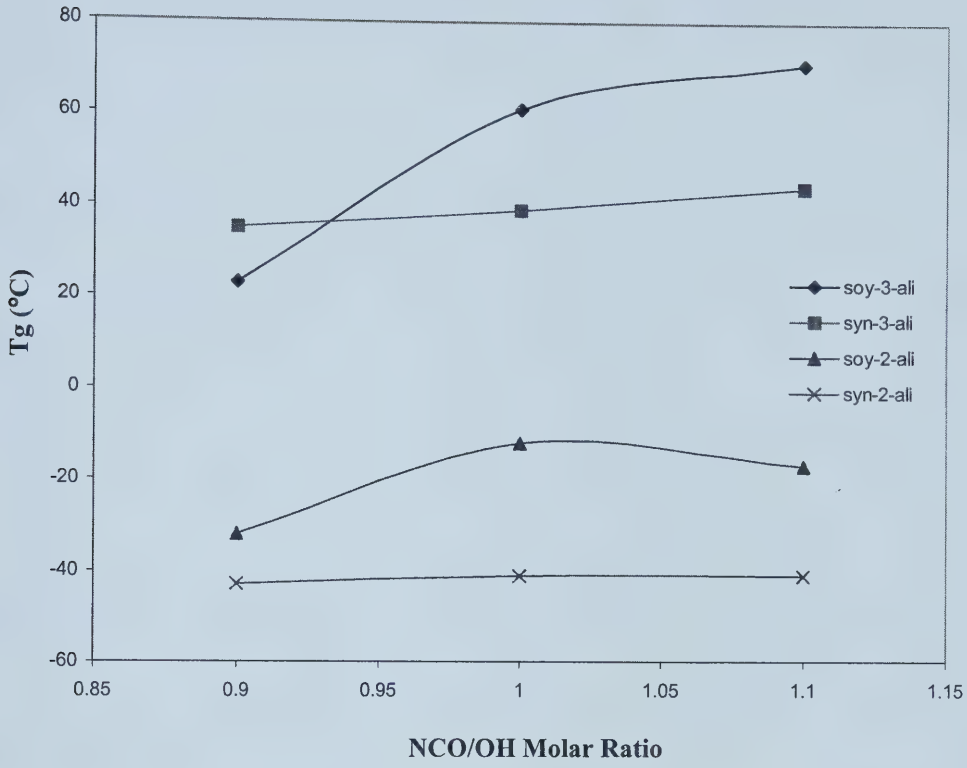


Figure 4.15 The Effect of Molar Ratio on Tg for the Aliphatic Polyisocyanate Formulations

As can be seen in Figure 4.14, for a given functionality of the polyol, the T_gs for the films are insensitive to the type of polyol used. However, this is not the case for the aliphatic polyurethanes. It was observed that the T_gs of the films made by aromatic polyisocyanate (either bi- or tri- functional) are slightly higher than those of aliphatic polyisocyanate. It should be noted that the T_gs of the films made by aromatic polyisocyanate and soy-based polyols are not necessary higher than those made by

aliphatic polyisocyanate and soy-based polyols. This is probably due to the steric hindrance in both aromatic polyisocyanates and soy-based polyols that lead to poor crosslinking.

4.6 Study on Chemical Structure of Selected Coating Films by FTIR

Fourier transform infrared (FTIR) spectroscopy is widely used in the coating industry for the analysis of coating components, drying process, interface reaction, and so on. Here, FTIR was also used to study the molecular structures of the films formed in an attempt to correlate such structure to the observed properties. Owing to the limited availability of FTIR spectrometer, tests were only performed on selective formulations. And they include formulations Soy-3-Ali (1.1), Syn-3-Ali (1.1), Soy-3-Aro (1.1), Syn-3-Aro (1.1) and Soy-3-Ali (0.9). The test results are shown in Figure 4.16 – Figure 4.20.

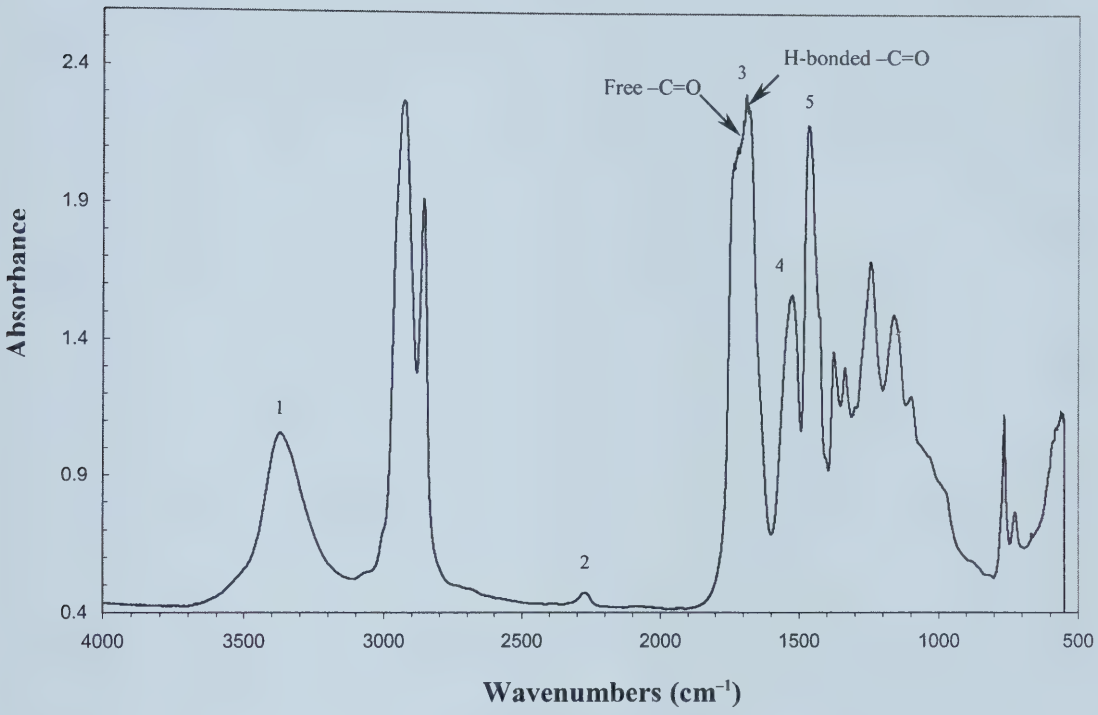


Figure 4.16 FTIR Spectrum for the Soy-3-Ali Formulation at a NCO/OH Molar Ratio of 1.1/1.0

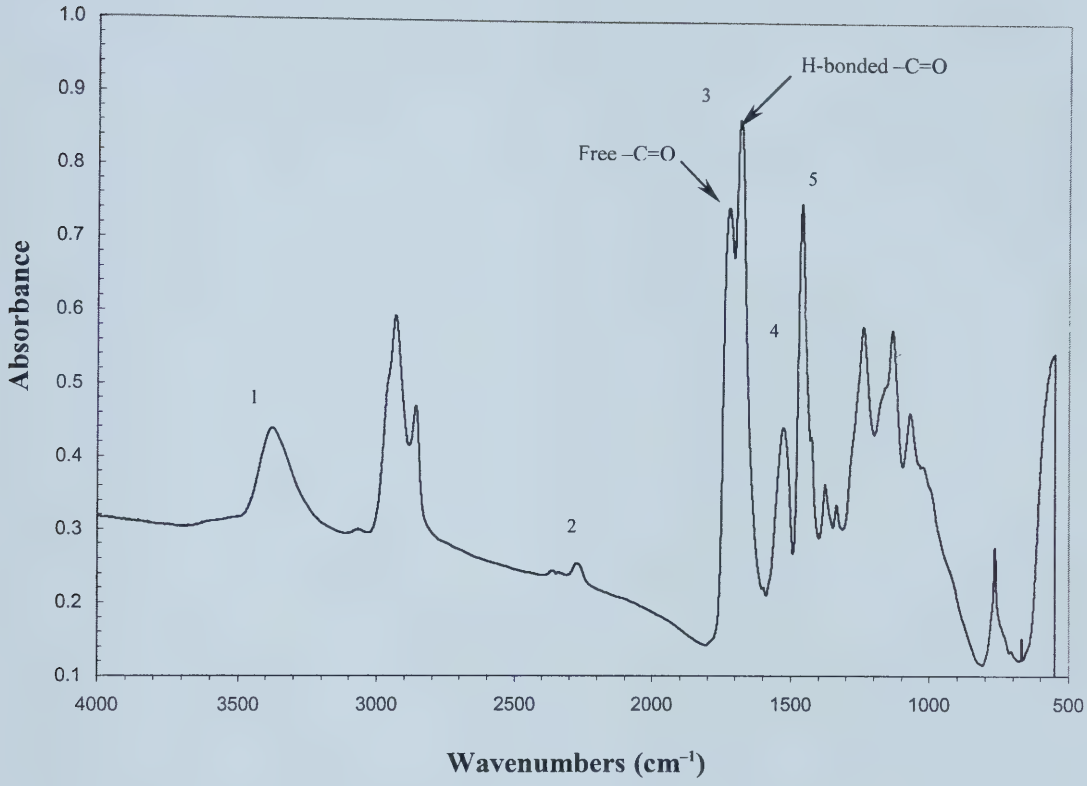


Figure 4.17 FTIR Spectrum for the Syn-3-Ali Formulation at a NCO/OH Molar Ratio of 1.1/1.0

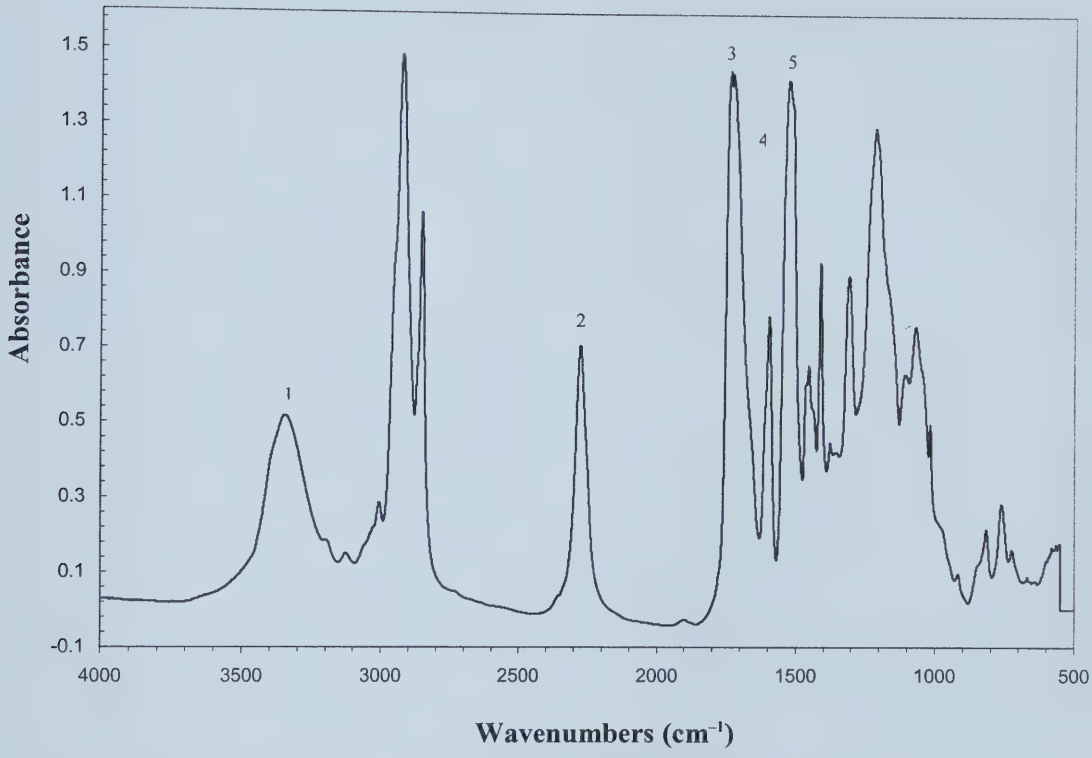


Figure 4.18 FTIR Spectrum for the Soy-3-Aro Formulation at a NCO/OH Molar Ratio of 1.1/1.0

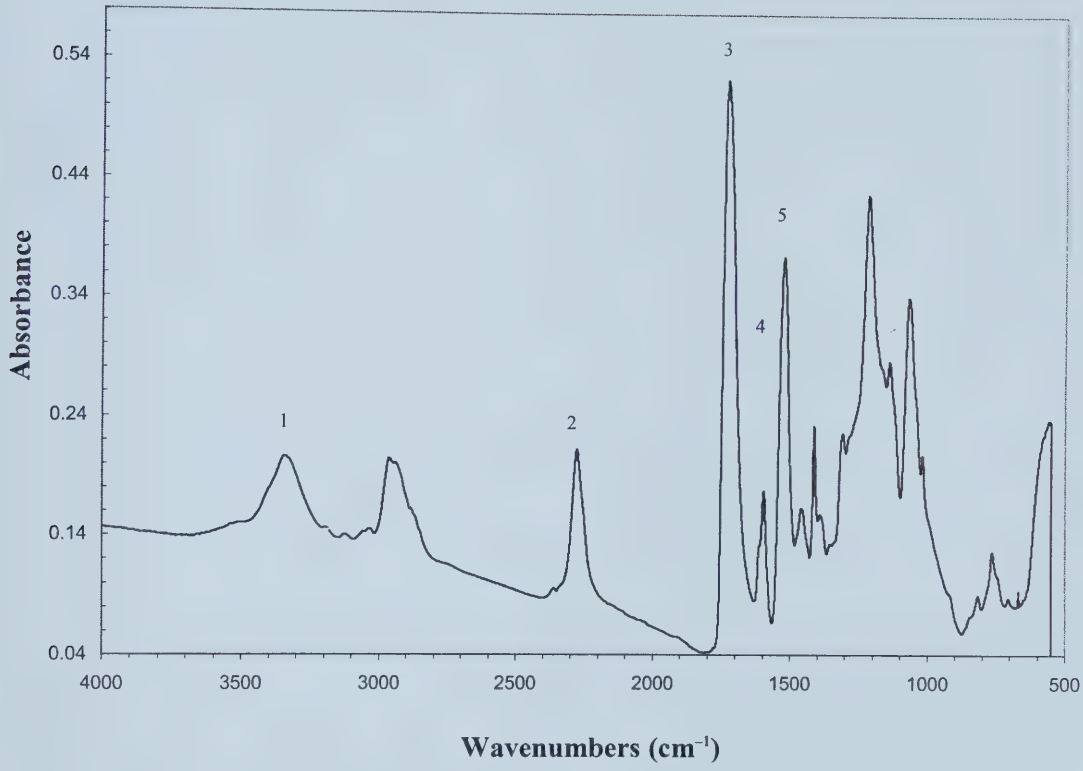


Figure 4.19 FTIR Spectrum for the Syn-3-Aro Formulation at a NCO/OH Molar Ratio of 1.1/1.0

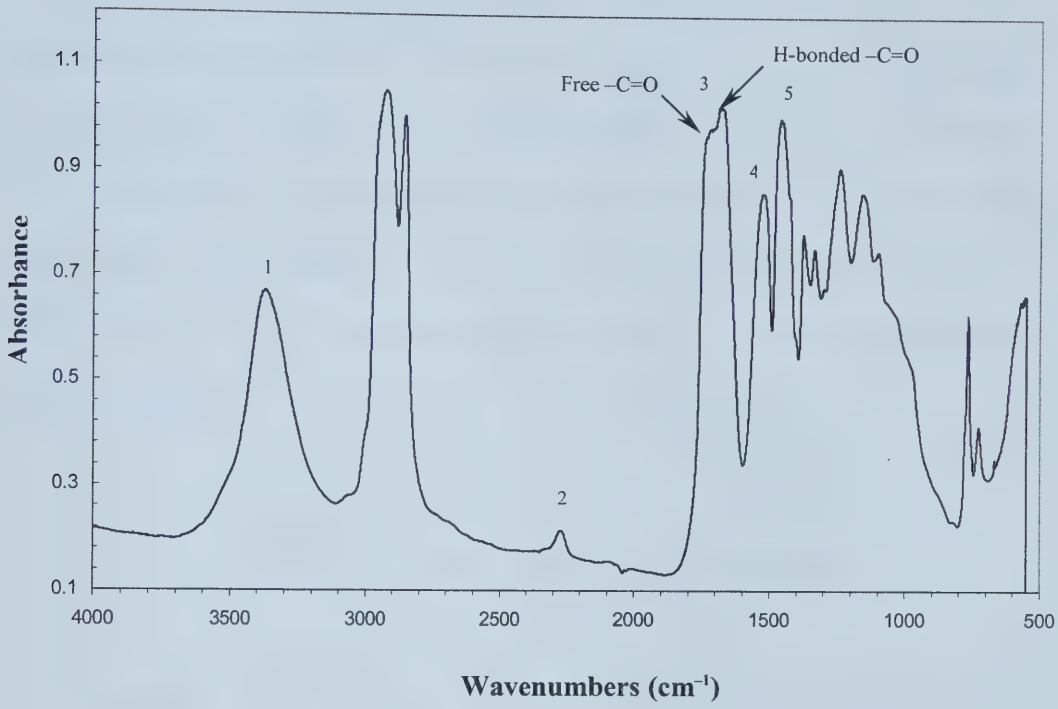


Figure 4.20 FTIR Spectrum for the Soy-3-Ali Formulation at a NCO/OH Molar Ratio of 0.9/1.0

In all FTIR spectra, the peaks that characterize the structures of the materials are marked with numbers (1–5). The characteristic peaks for polyurethane include the –N–H stretching vibration around 3300 cm^{-1}, the amide I region (i.e., –C=O stretching vibration) around 1700 cm^{-1}, amide II region (–NH– bending mode) around 1550 cm^{-1} and amide III region (–NH– bending mode) around 1450 cm^{-1}. More often, researchers use the –N–H and –C=O stretching vibrations to characterize

polyurethanes (Yu et al., 1999). In our FTIR spectra, Peak 1 corresponds to the –N–H stretching vibration; peak 2 the –NCO functional group; peak 3 the –C=O stretching vibration; and both peaks 4 and 5 amide bending vibrations. As shown in the figures, the intensities of the peaks differ. Since the intensities of the peaks are proportional to the concentrations of the corresponding functional groups, we can compare the magnitudes of the intensities of the peaks to infer the differences between the formulations. For easy viewing, the position and intensity of the important peaks are listed in Table 4.5.

Table 4.5 Location and Intensity of FTIR Peaks

Formulation	Peak 1		Peak 2		Peak 3		Peak 4		Peak 5	
	L.	I.	L.	I.	L.	I.	L.	I.	L.	I.
1.soy-3-ali (1.1)	3370	0.64	2270	0.02	1692	1.89	1525	1.15	1468	1.77
2.syn-3-ali (1.1)	3378	0.13	2270	0.04	1687	0.72	1529	0.30	1463	0.62
3.soy-3-aro (1.1)	3348	0.54	2278	0.76	1737	1.48	1597	0.82	1529	1.45
4.syn-3-aro (1.1)	3342	0.07	2277	0.12	1731	0.48	1597	0.13	1524	0.33
5.soy-3-ali (0.9)	3370	0.47	2273	0.04	1680	0.86	1525	0.68	1460	0.82

Note: Abbreviations L. — Location (wavenumber, cm^{-1}); I. — intensity.

Compared with formulations 1 and 2, we found that the intensities of all peaks except peak 2 in formulation 1 are much higher than that of the corresponding peaks in formulation 2. This indicated that the concentration of the urethane linkages in the film prepared from formulation 1 is much higher than that of formulation 2. This is also supported by the fact that the intensity of peak 2 of formulation 2 is higher than that of formulation 1, indicating that formulation 2 contained more un-reacted –NCO groups than in formulation 1. Since excess –NCO groups could further react with urethane linkages to form allophanates, and the film from formulation 1 contained more such linkages, its rigidity was higher than that of formulation 2. This result is consistent with the measured T_g of the corresponding films.

In both Figures 4.16 and 4.17, peak 3 was observed to split into two small-branched peaks. The splitting peaks around 1700cm^{-1} indicated the presence of hydrogen bonded urethane carbonyl groups. The wave number of hydrogen bonded –C=O groups is usually lower than that of non-hydrogen bonded –C=O groups (Tien et al., 2001; Yu et al., 1999). As can be seen in Figure 4.16 (formulation 1), the position and intensity of hydrogen bonded –C=O peak are 1692 cm^{-1} and 1.89, respectively, while those of formulation 2 (Figure 4.17) are 1687 cm^{-1} and 0.72, respectively. It is obvious that, the intensity of the hydrogen bonded –C=O peak of formulation 1 is much higher than that of formulation 2. Since the presence of hydrogen bonds would make the material dissipate energy without breaking covalent bonds as discussed in Section 4.3, formulation 1 exhibited higher abrasion resistance than formulation 2. Nonetheless, there is no peak splitting for peak 3, in Figures 4.18 and 4.19 (i.e., aromatic

polyisocyanate formulations with the use of the same polyols used in formulations 1 and 2). This indicated that either no hydrogen bonded –C=O groups exist or the concentration of hydrogen bonded –C=O groups was too low to be detected. In other words, the hydrogen bonding is weak in the polymers prepared by formulations 3 and 4. This is probably caused by the steric hindrance of the aromatic rings, which blocked the inter-molecular contact that is needed for hydrogen bond formation.

Comparing formulation 1 with 5, it is readily recognized that the intensity of the peaks that characterized the urethane linkages decreased with increasing NCO/OH molar ratio. The lower the NCO/OH molar ratio was, the less the urethane linkages formed. This also confirmed the fact that the mechanical properties of the film made by formulation 5 were not as good as those of the film made by formulation 1.

In summary, FTIR spectroscopy gives useful information about the molecular structure of the polymer used in a coating system. But such analysis is only qualitative, not quantitative and sometimes may be misleading. For example, the analysis of excess –OH groups cannot be performed because the –OH vibration region (around 3,440 cm^{-1}) (Guo et al., 2000) and –NH vibration region (around 3,400 cm^{-1}) overlap. Hence, the intensity of –NH groups shown in a FTIR spectrum, actually includes the un-reacted –OH groups. In order to obtain more structural information about the coating, other methods, such as nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry (MS), should be used (Golton et al., 1992).

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Chapter 5

Conclusions and Future Work

5.1 Conclusions

All the films made by aliphatic polyisocyanate showed better appearances than those by aromatic polyisocyanate, regardless of the type of polyol used. For aliphatic polyurethane, the type of polyol affected the film appearance greatly. In particular, films made by soy-based polyols showed good appearance. They were shiny and smooth. More importantly, they contained no bubbles and dents. On the other hand, aliphatic polyurethane films made by the synthetic polyols exhibited uneven shrinkage and contained many bubbles. Both tri-functional polyols and bi-functional soy-based polyol produced rigid films.

The adhesion performance of various coating formulations was also investigated. Basically, the adhesion performance was determined by the ability of the formulation to wet the substrate. The films made by tri-functional polyols showed extremely good adhesion to steel substrate while the adhesion strengths of the films made by bi-functional polyols were not so good. The NCO/OH molar ratio also influenced the adhesion performance of the coating films.

It was observed that the abrasion resistance of the coating films was strongly affected by the chemical and hydrogen bonding formed in the resultant materials. The films made by tri-functional polyols, either soy-based or synthetic ones, showed good abrasion resistance even at low NCO/OH molar ratios. But for the films made by bi-

functional polyols, their abrasion resistance showed different trends depending not only on the NCO/OH molar ratio, but also the polyisocyanate structure. At low NCO/OH molar ratios (e.g., 0.9/1.0), films made by aliphatic polyisocyanate and bi-functional polyols have lower abrasion resistance, but the films made by aromatic polyisocyanate and bi-functional polyols have higher abrasion resistance. At high NCO/OH molar ratios (i.e., 1.1/1.0), the situation was opposite.

In general, the water resistance performance of the films is influenced by the molecular polarity, hydrogen bonding and crosslinking density. Generally speaking, the water resistance of all films studied in the present work was high. At high NCO/OH molar ratios (e.g., 1.1/1.0), the films made by aliphatic polyisocyanate showed high water resistance, regardless of the polyols used. The maximum water absorbance of the films made by aromatic polyisocyanate was slightly higher than that of the films made by aliphatic polyisocyanate. However, it is still adequate for most coating applications. Nonetheless, the lower the NCO/OH molar ratio was, the higher the water absorbance was.

The thermal properties of the films were investigated by measuring their glass transition temperatures. The results indicated that some films were very rigid (T_g = 86 °C), and some were very elastic (T_g = –43 °C). In general, the films made by soy-based polyols showed higher T_gs than those made by synthetic polyols. The tri-functional polyols yielded rigid films while bi-functional polyols elastic films.

FTIR spectra of selected coating films were obtained to illustrate the structural difference of the polyurethanes made by different raw materials used in the present

work. Peaks that corresponded to the –N–H and –C=O stretching appeared in all FTIR spectra, indicating that urethane linkages were formed. The presence of splitting peaks in two spectra indicated that hydrogen bonds were formed in the films made by aliphatic polyisocyanate and tri-functional polyols.

Finally, it was concluded that soy-based polyols could be used as a film forming material. In some cases, the resultant coatings showed better properties than synthetic polyols with similar equivalent weight and functionality.

5.2 Future Work

First of all, all of the coating systems were prepared at 60 °C without the use of catalysts. This may not be convenient for certain practical applications that require room temperature curing. Since the addition of catalysts could alter end use properties of a coating. It is necessary to study the catalysts effect. This will be done in the future work.

In the discussion of the film qualities, some descriptions of the film appearances were qualitative and not very precise, such as hardness and shrinkage. In fact, the magnitudes of hardness and shrinkage could be measured. Further tests are required for these properties. Also, it is well known that the film quality is related to the film texture, which is determined by the microscopic structure. Therefore, scanning electron microscopy (SEM) micrographs should be obtained.

When the adhesion, abrasion resistance and water resistance of the films were discussed, structural information on crosslinking density, hydrogen bonding etc., was

needed to discern the observations. Various analytical techniques such as FTIR, NMR, dynamic mechanical analysis (DMA) etc., should be used to fully characterize the structures.

Appendix A

Sample Calculations

1. NCO/OH molar ratio = 1.0/1.0.

   For the aliphatic polyisocyanate, its equivalent weight is 133 (see Table 2.1). This means that 133 g of aliphatic polyisocyanate contains 1 mole of –NCO groups.

   For the tri-functional soy-based polyol, its equivalent weight is 204 (see Table 2.4). This means that 204 g of tri-functional soy-based polyol contains 1 mole of –OH groups.

   Therefore, when NCO/OH molar ratio is set at 1.0/1.0, one needs to mix 133 g of aliphatic polyisocyanate with 204 g of tri-functional soy-based polyol to obtain a polyurethane with the required molar ratio.

2. NCO/OH molar ratio = 1.1/1.0.

   The amount of aliphatic polyisocyanate needed is: $133 \times 1.1 = 146.3$ (g)

   The tri-functional soy-based polyol needed is still 204 g.

3. NCO/OH molar ratio = 0.9/1.0.

   The aliphatic polyisocyanate needed is: $133 \times 0.9 = 119.7$ (g)

   Tri-functional soy-based polyol needed is: 204 g.

For all other formulations, the calculations are exactly the same as what is shown above.

Appendix B

DSC Curves for Aromatic Polyurethanes

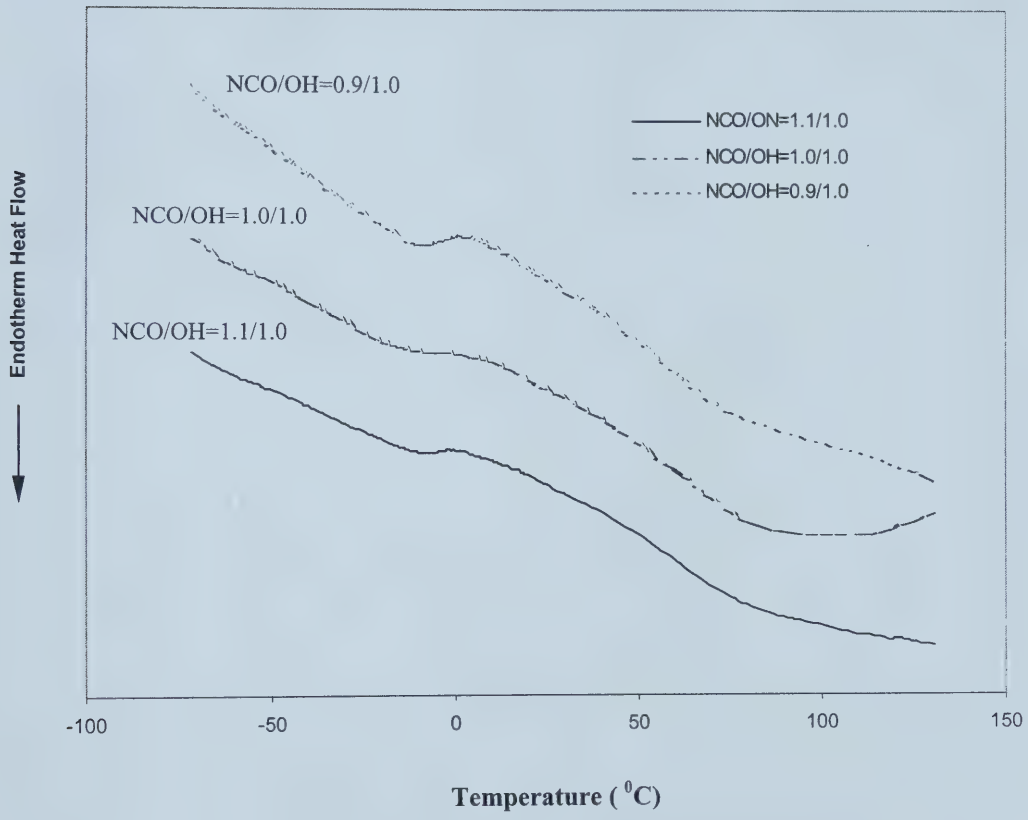

Figure B1 DSC Curves for Soy-3-Aro Films at Different NCO/OH Molar Ratios

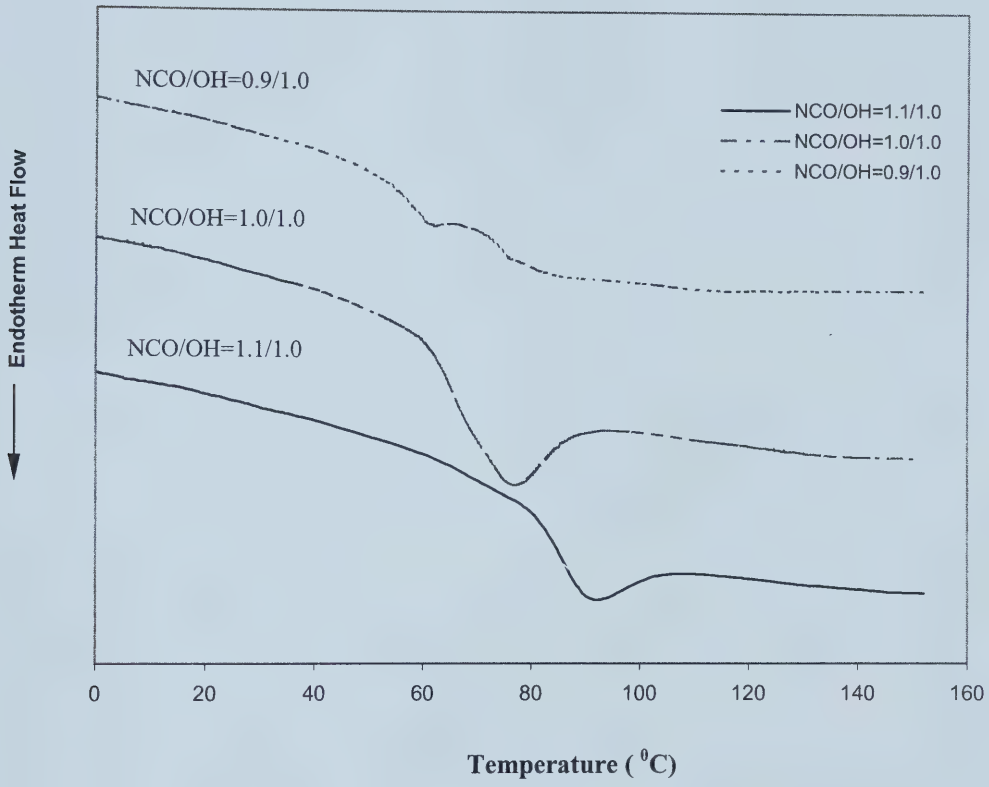

Figure B2 **DSC Curves for Syn-3-Aro Films at Different NCO/OH Molar Ratios**

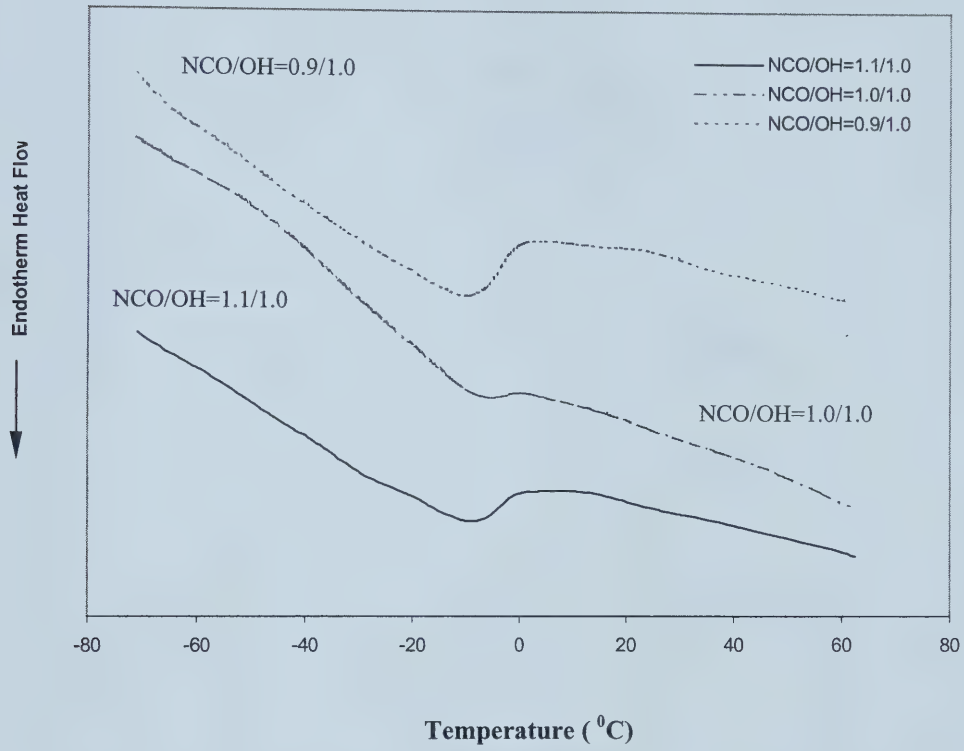

Figure B3 DSC Curves for Soy-2-Aro Films at Different NCO/OH Molar Ratios

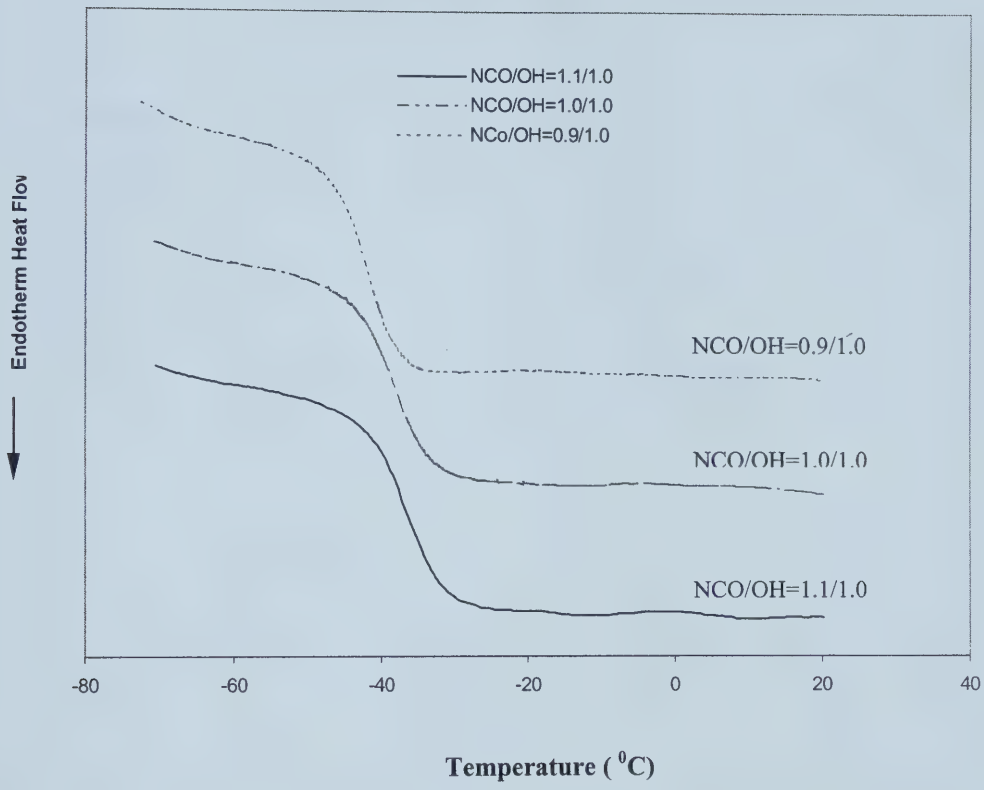

Figure B4 DSC Curves for Syn-2-Aro Films at Different NCO/OH Molar Ratios

Table B1 **T_g of the Polyurethane Coatings Made by Aromatic Polyisocyanates at Different NCO/OH Molar Ratios**

NCO/OH Molar Ratio	Tg for Soy-3-Aro	Tg for Syn-3-Aro	Tg for Soy-2-Aro	Tg for Syn-2-Aro
1.1/1.0	59	86	-34	-37
1.0/1.0	65	66	-37	-39
0.9/1.0	59	58	-35	-42

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